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DEVELOPMENT OF THE 2007 CHEMICAL DECONTAMINANT SOURCE DOCUMENT

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14. ABSTRACT:
The chemical decontaminant performance evaluation testing source document is the product of project BA06DEC414 for improved test methodology. The primary objective is to improve the rigor of existing test methods for the generation of defensible and comparable decontamination efficacy data for the quantitative determination of post-decontamination contact and vapor hazards and residual agent. Execution of these improved methods will yield higher fidelity data presented in appropriate context. The data generated from these updated methods enhance all components of the decontaminant life cycle, including research and development (R&D), science and technology (S&T), testing and evaluation (T&E), developmental and operational testing (DT/OT) activities, and technology readiness assessments (TRAs) to determine technology readiness level (TRL), technology comparisons, risk assessments, and milestone decisions. The document also includes updates to several of the material compatibility tests that were updated to support program BA06DET504. This report provides a summary of the key experimental testing conducted to develop the methods in the Source Document.

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PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency Joint Science and Technology Office (DTRA JSTO) project BA06DEC414. The work was started in March 2006 and completed in December 2007.

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CONTENTS

1. INTRODUCTION 1

2. SD 3

2.1 Chemical Biological Decontaminant Testing TOP 3
2.2 Decontaminant Venn Diagram 4
2.3 Chemical Decontaminant Performance Evaluation SD 4
2.4 SD Overview 5

3. PANEL TEST UPDATE 6

3.1 Coupon Treatment 6
3.2 Remaining Agent Test 7
3.3 Contact Test 7
3.4 Vapor Test 8
3.5 Extraction Efficiency 8
3.6 Supporting Analytical 9

4. MATERIAL COMPATIBILITY TESTING 2007 UPDATE 10

4.1 Metal Corrosion Test Method 11
4.2 Elastomer Sorption and Hardness Test Method 12
4.3 Thermoplastic Sorption, Haze, and Transmittance Test Method 13
4.4 Hardness (Coating) Test Method 13
4.5 Guidance for the Use of Standardized Test Methods for Decontaminant Evaluations 13
4.6 pH Measurement 14

5. TEST METHODS NOT PENDING UPDATE IN 2006–2007 PROGRAM 15

5.1 Chemical Kinetics Determination via Stirred Reactor Test 15
5.2 Test Planning and Design 15
5.3 Rinsate Analysis 15
5.4 Detection and Protection Methods 17
5.5 Decontaminant Pot- and Shelf-Life Methods 17

LITERATURE CITED 19
ACRONYMS 21

APPENDIX: 2007 SOURCE DOCUMENT 23

Section 1: Introduction 27
Section 2: Test Planning, Considerations, and Requirements 33
Section 3: Decontaminant Preparation and Properties 35
Section 4: Chemical Kinetics Determination via Stirred Reactor Test 43
Section 5: Material Compatibility Testing 49
Section 6: Panel Contact Test to Determine Contact Hazard 65
Section 7: Panel Vapor Test to Determine Vapor Hazard 237
Section 8: Detection and Protection Test Methods 363
Sub-Appendix A: Acronym List and Glossary 371

Sub-Appendix B: 2002 TOP Suggested Material and Contaminant List 381
Sub-Appendix C: 2007 Low-Level Analytical Methods 387

FIGURES

1. Decontaminant Venn diagram depicting material, agent, and decontaminant interactions 4
2. Coupon treatment and remaining agent sampling representation 9
3. Coupon treatment and contact sampling representation 10
4. Coupon treatment and vapor sampling representation 10
5. Decontamination Venn diagram showing material, agent, and decontaminant relationships 11
6. Decontaminant Venn diagram highlighting agent-decontaminant interaction 16
7. Chemical kinetic versus endpoint determination representation 16

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DEVELOPMENT
OF THE 2007 CHEMICAL DECONTAMINANT SOURCE DOCUMENT

1. INTRODUCTION

If contamination occurs, there is the need to reduce the risk to personnel and equipment while maintaining the ability to complete the mission. There are four levels of decontamination: immediate, operational, thorough, and clearance.[1] Each level has specific objectives and specifications for the reduction of contamination. Immediate decontamination occurs within 15 min of contamination with an emphasis on saving lives and limiting contamination spread. Operational decontamination is performed to sustain operations by reducing the spread of contamination and providing temporary relief from long-term mission oriented protective posture (MOPP). FM 3-11.5 recommends that operational decontamination be initiated within 1 h for chemical agent resistant coating (CARC) coated surfaces and within 6 h for non-CARC surfaces. Thorough decontamination is the significant reduction in contamination level for long-term MOPP reduction. Thorough decontamination is initiated when the mission allows; however, the field manual recommends an initiation time as short as possible as many decontamination techniques become less effective over time. Clearance decontamination is the reduction in contamination to a level that allows for unrestricted use, transportation, or disposal. To support field needs, decontaminants are evaluated through a development and testing process.

Decontaminant development and testing typically focuses on thorough decontamination identifying decontaminants that can significantly reduce contamination in a short period of time that are safe to personnel and equipment. In the decontamination business area (now called hazard mitigation), all emerging decontaminants and technologies are required to demonstrate the ability to meet a specified set of key performance parameters (KPPs) per the acquisition program Operational Requirement Document (ORD). One of the specific KPPs to be demonstrated is that of chemical agent decontamination efficacy. The chemical agent efficacy determination is accomplished through the execution of the standard panel contact and vapor tests as documented in Test Operations Procedure (TOP) 8-2-061. At the research and development (R&D) stages of 6.2 and 6.3, these tests provide the data set that is evaluated during transition activities such as the Technology Readiness Assessment (TRA) to determine the technology readiness level (TRL) and to support Milestone A and B decisions. Similarly, developmental and operational testing (DT/OT) uses these same test procedures post milestone B for TRLs 7 through 9.

The data generated from the science and technology (S&T) and DT/OT must be defensible and comparable to identify the next generation technologies and support acquisition transition tasks such as TRAs, milestone reviews, and third party data evaluations. Historical test documentation is often of limited value due to lack of thorough documentation regarding test design, execution, and quality control (i.e., testing conditions, use of control tests, analytical Continuing Calibration Verification (CCV) samples, and data acceptance procedures). The comparison of decontaminant test data from different laboratories or for different technologies has been limited to approximations as the current test protocols are not detailed enough and documentation requirements are limited preventing the ability to easily compare data and provide the full context of the test conditions. The inability to compare data creates management challenges for the selection of the best decontaminant technology for an acquisition program. The lack of specific methods and data utilization limitations often result in the need for additional testing.

The past approaches for decontaminant technology development and testing are further challenged by the lack of data calculation methodologies. As a result, different test facilities may perform data calculations in different ways to determine if a technology meets a requirement such as a contact or vapor hazard. The method and calculation vagueness creates a range of results from technologies that may perform well in some aspects, but may overlook advantages, limitations, or caveats in the data. As the need for product development on shortened time schedules and reduced funding increases, there is a

need to collect accurate data that can be compared to requirements and other decontaminants to support management reviews. The methodology should be rigorous to enable data comparisons with enough flexibility to enable testing at different conditions and stages and with different technologies. The combination of rigor and flexibility is enabled through thorough documentation of what was tested, how it was tested, and uniform treatment of the data to provide the necessary context required to properly interpret the data. The need for additional testing can be minimized by identifying the objectives of the acquisition program and performing the tests that address the needs and KPPs of the program.

Defense Threat Reduction Agency (DTRA) Joint Science and Technology Office (JSTO) program BA06DEC414 is the foundation toward change by first improving the test structure, which is used to perform the decontamination mission. DTRA program BA06DEC414 was initiated in FY06 to update these methods. The primary objective was to improve the rigor of existing test methods for the contact and vapor test from TOP 8-2-061 "Chemical Biological Decontaminant Testing" for the generation of defensible and comparable decontamination efficacy data for the quantitative determination of post-decontamination contact and vapor hazards and residual agent. Execution of these improved methods will yield higher fidelity data presented in an appropriate context. The data generated from these updated methods enhance all components of the decontaminant life cycle including R&D, S&T, testing and evaluation (T&E), and DT/OT activities, TRAs to determine TRL, technology comparisons, risk assessments, and milestone decisions. This program has utilized practices from Business Process Reengineering (BPR) and recognized international standards (e.g., ASTM, ISO) during the effort. The BPR is a management approach aiming at improvements by means of elevating efficiency and effectiveness of the processes under investigation. These tools are applied to this program by systematically evaluating the test processes and identifying the variables that have the greatest impact on the test results, more specifically, by determining the resulting post-decontamination hazard.

The format used to document the test method improvements was designed to ensure that all of the necessary elements were captured. The Chemical Decontaminant Performance Evaluation Source Document (SD) was a product from this program. The SD format uses a blend of scientific text book educational format and required ASTM and ISO fields. The scientific text book approach informs the reader regarding the test purpose, test limitations, and other associated tests, so proper tests can be selected based on program objectives. For example, decontamination methods include neutralization, physical removal, and weathering. Neutralization is the reaction of the contaminant and decontaminant material to produce a reaction product that is of lower toxicity compared to the original contaminant. Physical removal is the relocation of the contamination from the surface of interest to a surface of lesser importance. Weathering includes processes such as evaporation. The SD provides guidance on which test to execute and specifies how to calculate each of these values. Most decontaminants and decontamination processes use a combination of neutralization and physical removal. If a decontamination process used a prerinse process in addition to the decontaminant treatment, some of the contamination may be physically removed. If the program objective was to achieve a high degree of chemical neutralization, then the rinse water must be collected and analyzed to determine the amount of contaminant that was relocated. Failure to collect and analyze the rinsate could give a false confidence that a high degree of neutralization occurred. The SD contains detailed data calculation methods. Each test also includes acceptance criteria and discusses the impact of the major system variables. The text book style is used to demonstrate specific calculation methods using small sets of data. The use of ASTM and ISO fields enable performing laboratories to introduce these methods into their quality systems.

The 2007 Chemical Decontaminant Performance Evaluation SD contains the updated contact- and vapor-test methodology. The contact test chapter includes specific test methodology for determining the remaining agent and performing the contact test, including supporting methods for extraction efficiency determinations and chromatographic analysis. The test procedures contain options allowing for test modifications and guidance on how those modifications may impact data calculations. The contact test chapter contains detailed data calculations for determining percent efficacy, percent

neutralization, and contact hazard. The calculations are further divided into calculated, approximated, or inferred calculations. These divisions are based on the availability of required data and indicate the degree of rigor used to calculate the result.

The vapor hazard test underwent the most significant improvement. The method for calculating vapor hazard was historically based on the vapor concentrations directly measured in the vapor chamber. The result is often an overestimation of the hazard. Overestimating the resulting hazard can impact decontamination development resulting in greater logistical requirements and increased potential for material incompatibilities. In addition, the comparison of chamber vapor concentration to a requirement to determine if a toxicological response will occur was not correct. The documented methods are now aligned with the Department of Defense (DoD) accepted method for the determination of a vapor exposure using a toxic load calculation.[2] This calculation does require the specification of a scenario for complete analysis. This new calculation method is demonstrated using a small set of sample data and six example scenarios.

For completeness, the SD also contains relevant methodology improvements from other programs and other TOP 8-2-061 tests not updated as part of this program. The low-level analytical methodology developed under program CA06DEC407 is included. The TOP 8-2-061 methods not updated during the FY06–07 program include the chemical kinetics determination via stirred reactor test, convective flow for air permeable materials test, detector compatibility test with decontaminant, individual protective equipment, and collective protective equipment compatibility tests. These SD sections contain the procedures directly from TOP 8-2-061 (2002 release). In addition, suggestions are provided for test preparation and documentation because no new data was collected to evaluate the test procedure.

This SD will have an FY08 program update to include the further method developments from DTRA JSTO programs CA08DEC420 and CA07DEC499. One of the components of CA08DEC420 is the development of a decontaminant development model to facilitate R&D test planning and maturity determinations. The CA07DEC499 program is an extension of the methodology program aimed at establishing contact and vapor testing for small items of sensitive equipment. These methods have direct application to upcoming DT/OT for the Joint Material Decontamination System (JMDS) acquisition program and Joint Tactical Decontamination System – Large Scale (JSTDS-LS) programs of record.

The method development activities were performed from March 2006 to December 2007 in the Decontamination Sciences Team laboratories at the U.S. Army Edgewood Chemical Biological Center (ECBC), Aberdeen Proving Ground (APG), MD. The chemical decontaminant method development overview is presented in this report. The 2007 Chemical Decontaminant SD is included intact as an appendix. The detailed development of the contact- and vapor-test methodology is documented under a separate cover and is referenced within this report.

2. SD

2.1 Chemical Biological Decontaminant Testing TOP

TOP 8-2-061, Chemical Biological Decontaminant Testing is the collection of test procedures commonly used to evaluate decontaminants.[3] TOP 8-2-061 contains procedures for evaluating kinetics, decontaminant endpoint, contact and vapor hazards, material, detector, and protective equipment compatibility. The document serves as a good starting point collecting the relevant procedures in a single test document accessible to all research, development, and test personnel. Based on the challenges associated with lab-to-lab and test-to-test comparisons and data traceability, the need to increase the rigor was recognized. To capture the improvements, the SD format was developed.

2.2 Decontaminant Venn Diagram

The Decontamination Venn Diagram is used to represent three elements to decontaminant testing and common tests used to evaluate interactions (Figure 1). The three elements are agent (i.e., contaminant), material contaminated, and decontaminant. The stirred reactor chemical kinetics and endpoint test evaluate the interaction of the agent and decontaminant in the absence of material effects. The most common decontaminant–material interaction evaluation is material compatibility tests to determine the impact the decontaminant has on material integrity. Material properties influence the way an agent interacts with the surface. The primary agent–material interaction of concern in decontamination testing is sorption. The panel test evaluates all three interactions to determine the decontaminant performance for reducing the agent contamination on specific materials. All of these elements and interactions are affected by environment.

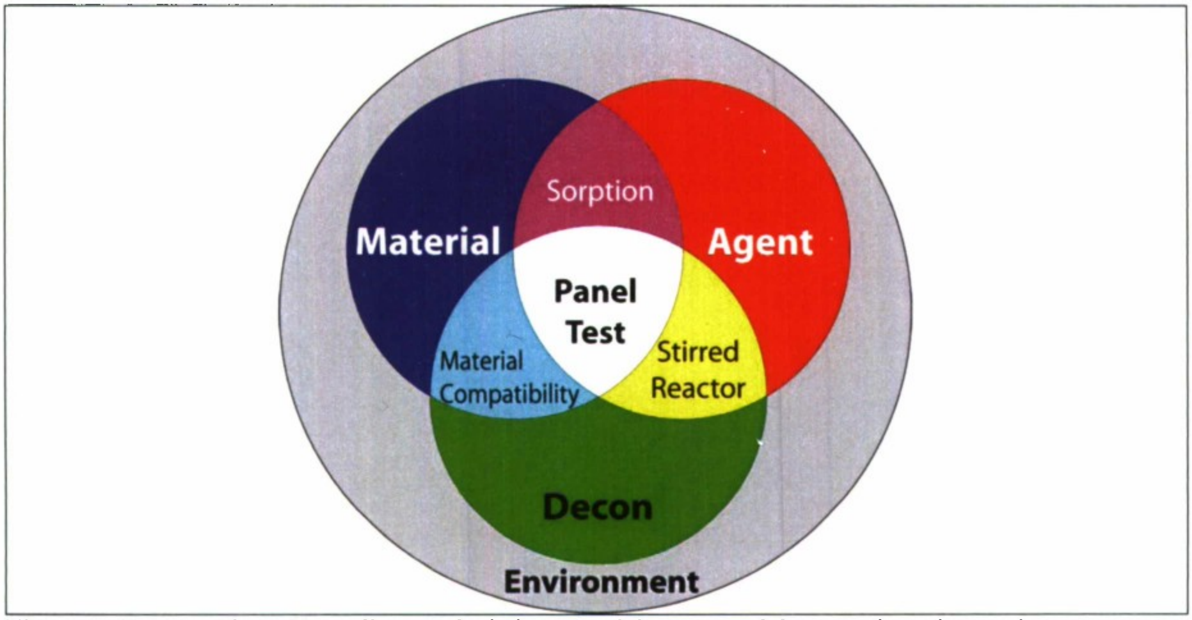

Figure 1. Decontaminant Venn diagram depicting material, agent, and decontaminant interactions.

2.3 Chemical Decontaminant Performance Evaluation SD

The Chemical Decontaminant Performance Evaluation SD is the product of project BA06DEC414 for improved test methodology. The primary objective was to improve the rigor of existing test methods from TOP 8-2-061 "Chemical Biological Decontaminant Testing" for the generation of defensible and comparable decontamination efficacy data for the quantitative determination of post-decontamination contact and vapor hazards and residual agent. Execution of these improved methods will yield higher fidelity data presented in an appropriate context. The data generated from these updated methods enhance all components of the decontaminant life cycle including R&D, S&T, T&E, and DT/OT activities, TRAs to determine TRL, technology comparisons, risk assessments, and milestone decisions. The document also includes updates to several of the material compatibility tests that were updated to support program BA06DET504. The appendix contains the analytical methodology developed under program CA06DEC407.

2.4 SD Overview

The SD organization uses a text book chapter and section structure. Each chapter is focused on a specific topic, such as test planning, decontamination preparation, contact-test method, vapor-test method, etc. Each chapter is divided into sections for each task supporting that topic.

The test method is a basic research procedure outline including reagents, materials, procedure, calculations, and reporting. The basic foundation was augmented by incorporating the elements required by ISO-17025 and ASTM methods such as procedure summary, terminology, reporting criteria, quality assurance (QA)/quality control (QC), and test acceptance criteria. This format facilitates method insertion into performing laboratory quality systems. Each test section carries relevant terminology, references, calculations, and QA/QC requirements, so each chapter subsection can be used as an independent method. The SD contains a test planning chapter, six test method chapters, and associated appendices. A general description of each chapter is provided in the following list:

- Section 2: Test Planning: The test planning section is anticipated to be developed in the FY08 program. This section will focus on setting objectives and selecting the appropriate tests to meet the stated objectives. The section will include test selection and data utilization guidance to benefit test directors, program managers, and other data users.
- Section 3: Decontaminant Preparation and Evaluation: This section contains the test methods for measuring decontaminant pH, pot life, and shelf life/accelerated aging.
- Section 4: Chemical Kinetics Determination via Stirred Reactor Test: The stirred reactor test is the evaluation of a decontaminant to neutralize agent under ideal conditions in that there are no material effects impacting decontaminant performance. The test is typically conducted for new decontaminant formulations compared to a reference decontaminant, typically household bleach.
- Section 5: Material Compatibility Testing: The material compatibility tests are used to determine the impact the decontaminant has on the intended material function. These tests are typically conducted materials that have not been contaminated with agent. These tests could be performed on materials that have been contaminated and decontaminated.
- Section 6: Panel Test to Determine Contact Hazard: The contact test series contains the procedures for the measurement of contaminant present after the decontamination process that could pose a hazard to unprotect personnel through skin or contact transfer to other surfaces. These tests use a contact sampler as a surrogate for human skin, coupons of operationally relevant surfaces of interest, solvent extraction, and chromatographic analytical methods. The rigorous laboratory-scale test method uses a standard 2 in. diameter circular coupon. The methods can be applied to larger coupons and test articles. These tests can be used to evaluate decontaminants in liquid, solid, or vapor form.
- Section 7: Panel Test to Determine Vapor Hazard: The vapor test series contains the procedures for the measurement of contaminant vapor present after the decontamination process that could pose a vapor hazard to unprotected personnel. These tests utilize a vapor chamber to capture contaminant vapor emissions from the material to calculate an emission factor, which is then used to determine the vapor hazard for the scenario. The rigorous laboratory-scale test method uses a standard 2 in. diameter circular coupon. The FY08 update will include methods for the evaluation of larger coupons and test articles. These tests can be used to evaluate decontaminants in liquid, solid, or vapor form.
- Section 8: Detection and Protection Test Methods: This section contains the test methods for convective flow for air permeable materials, detector compatibility test

with decontaminant, and individual protective equipment and collective protective equipment compatibility.

- Sub-Appendix A: Acronym and Abbreviation List: The acronyms and abbreviations used throughout this document for chemical decontaminant testing protocols are listed in this appendix. The acronyms and abbreviations are divided based on general categories. Laboratories using these methods should avoid using acronyms that overlap with document specific acronyms. All laboratory specific acronyms used in test documentation not listed in this appendix should be defined in the test plan and defined on first usage.
- Sub-Appendix B: Suggested Material and Contaminant List: This appendix contains information regarding coupon materials, contaminants, and decontaminants.
- Sub-Appendix C: Low-Level Analytical Methods: This appendix contains the methodology developed under program CA06DEC407 regarding the analytical methods to detect and quantify the contaminants (i.e., agent).

3. PANEL TEST UPDATE

The data generated from the S&T testing and DT/OT must be defensible and comparable in order to identify the next generation technologies and support acquisition transition tasks such as TRAs, milestone reviews, and third party data evaluations. The panel contact and vapor tests are highly utilized methods to assess a decontaminant performance compared to a requirement value. The test results are used to determine if a post-decontamination hazard is present for unprotected personnel. These data and hazard determination are used to make acquisition program technology selections. The approach was to develop test methodology with sufficient rigor to enable data comparisons with enough flexibility to enable testing at different conditions and using different technologies. The lab scale contact and vapor tests, which use small coupons representative of operationally relevant materials, were the primary focus. At the lab scale, most process variables can be controlled, and nearly all process variables can be measured. The control and measurement of the process variables enabled the identification of the variables that most affect data scatter and resulting hazard calculation. The tightest data should be achieved at the laboratory scale. If the lab method cannot achieve good test performance (i.e., reproducibility), it is likely that tests performed at larger scale and in real environments will produce results with such significant spread (i.e., variability) that it will not be possible to make quantitative or confident conclusions from the data, especially in regard to meeting requirements or comparing data. The identification and impact of the process variables were conducted using process isolation tests. The following subsections include a description of the test or process and an overview of the method update and accomplishments.

3.1 Coupon Treatment

The coupon treatment process for the remaining agent, contact, and vapor tests is shown in Figures 2, 3, and 4, respectively. As a brief overview of the process, the coupons are preconditioned to the desired environmental test condition. The coupons are contaminated with agent at the desired contamination challenge and deposition pattern (i.e., drop volume and drop spacing). The coupons are typically aged mimicking a minimum time to reach a thorough decontaminant line. The standard aging time is 60 min. Agent–material interactions involve mass transport processes such as sorption; the aging time is a test variable that can significantly affect the test results. The decontaminant is applied to the surface for a dwell time. The decontaminant process may or may not include pre- and/or post-decontamination rinse steps. The coupon is allowed to dry. At the end of the drying period, the decontamination treatment process is complete. The sample can then be evaluated using the remaining agent, contact, or vapor tests.

The panel test treatment determines the performance measured by the remaining agent, contact, and vapor tests. The treatment portion of the method needs to be robust enough that the

difference in decontaminant performance can be measured, not the variations of the method. The treatment method was evaluated early in the program through process isolation tests. Process isolation tests focused on measuring a component of treatment to determine how that component affects the final result. Contamination surface coverage, aging time, and temperature were several of the treatment parameters that can significantly affect the final result. The inability to control or measure the key variables results in significant data variability, which significantly complicates the interpretation or comparison of results to other tests.

3.2 Remaining Agent Test (SD Method 6-E)

The remaining agent test is the measurement of the total amount of contaminant present after the decontaminant treatment process. This test is preferred for the determination of the percent neutralization, reduction in starting challenge, and decontaminant comparison studies. After the panel test process, the coupon is placed in the appropriate extraction solvent for a specified period of time. An aliquot of the extraction solvent is analyzed using the appropriate analytical technique. The results are calculated using the procedures in SD Method 6-G.

Mass transport processes move the agent remaining after the decontaminant treatment back to the surface. The contact and vapor tests sample how the remaining agent is transported from the material to unprotected personnel to determine the contact and vapor hazards for the time period sampled. At the end of these tests, the coupon can then be extracted to determine the residual agent. If residual agent is present, a future hazard could exist. The process isolation and time length studies conducted demonstrated that residual agent does pose a hazard and time extrapolation of test results could give a false sense of a lower hazard or hazard duration for sorptive materials. The remaining agent test was developed to support early R&D activities and is the best suited test to answer questions regarding percent neutralization and reduction in starting challenge. The remaining agent test should be used in early R&D to measure the decontaminant capability for removing contaminant from the surfaces of interest. The remaining agent test imparts less burden on the testing facility including shorter tests (compared to contact and vapor testing), more throughput (fewer samples requiring analysis generated), and less waste generation and provides easy to interpret results enabling useful results with less financial and time burdens. Decontaminant development should focus on getting the agent out of the materials of interest. The contact and vapor tests should be conducted during later development to determine the hazard as a result of any agent the decontaminant could not remove or neutralize.

3.3 Contact Test (SD Chapter 6)

The contact test is the measurement of the contaminant present after the decontaminant treatment process that could pose a hazard to unprotected personnel by contacting (i.e., touching) the surface. This test is typically performed to compare decontaminant performance against requirement document specifications. The test uses a skin simulant that is placed on the surface for a specified period of time at a controlled temperature. This contact event is referred to as a touch. At the end of the touch, the contact sampler is placed in the appropriate extraction solvent for a specified period of time. At the end of the contact test, the residual contaminant remaining in the material can be measured by the residual agent test. The coupon is placed in the appropriate extraction solvent for a specified period of time. Aliquots of the extraction solvents are analyzed using the appropriate analytical technique. The contact process is shown in Figure 3. The results are calculated using the procedures in SD Method 6-G.

The contact test method had minimal updates to the general procedure. The procedure was expanded to provide greater detail for test consistency and additional rigor for key variables. The contact test chapter includes specific test methodology for determining remaining agent and performing the contact test including supporting methods for extraction efficiency determinations and chromatographic analysis. The test procedures contain options allowing for test modifications and how those modifications may impact data calculations. The contact test chapter contains detailed data

calculation for determining percent efficacy, percent neutralization, and contact hazard, which were not included in the original TOP. The calculations are further divided into calculated, approximated, or inferred calculations. These divisions are based on the availability of required data and indicate the degree of rigor used in the calculation. The updated methods are documented in SD Chapter 6.

3.4 Vapor Test (SD Chapter 7)

The vapor test is the measurement of the contaminant emission from the surface of interest to determine the vapor emission factor. This emission factor is used to determine if a vapor hazard would occur to unprotected personnel in a specified scenario. This test is typically performed to compare decontaminant performance against requirement document specifications. The coupon is placed in a vapor chamber and the off-gassing measured. An illustration showing the coupon in a vapor chamber and emitted vapor collected on a solid sorbent tube is shown in Figure 4. The solid sorbent tube is then analyzed using the appropriate analytical technique.

The vapor test underwent a major transformation as part of this effort. The method for calculating if a vapor hazard was present was historically based on the vapor concentration measured in the vapor chamber, which does not correspond to the vapor concentration to which unprotected personnel would be exposed. The result is often an overestimation of the hazard. Overestimating the resulting hazard can impact decontamination development resulting in greater logistical requirements and increased potential for material incompatibilities. In addition, the comparison of a test chamber vapor concentration to a requirement to determine if a toxicological response will occur was not correct. The DoD accepted method for the determination of a vapor exposure uses toxic load. The vapor test method was updated to include the information necessary to determine the material emission factor. This factor is needed to then determine the scenario vapor concentration and toxic load. The updated methods contain detailed calculations aligned with the DoD accepted method. This calculation does require a scenario for complete analysis. This new calculation method is demonstrated in the SD using a small set of sample data and six example scenarios. The determination of the emission factor from the emission source enables an initial scale-up calculation to determine the vapor hazard for specific items in scenarios of interest enabling initial identification of trade space and operational considerations. This method update is the foundation toward lab-data scale up to include estimated composite systems. An example composite system is a vehicle constructed from painted metal, glass, rubber, and elastomer. Combining the vapor test data for several materials in the appropriate proportions can give an initial assessment of actual item in the scenario. The small item test methods under development in program CA07DEC499 rely heavily on this foundation. These methods illustrate effects that should be considered in concept of operations (CONOPS) such that a single item may pass the decontamination efficacy requirement for vapor hazard. However, the combination of multiple decontaminated items may present a hazard in specific scenarios, such as movement into a vehicle or building interior space.

3.5 Extraction Efficiency (SD Methods 6-B, 6-F, 7-D)

The extraction efficiency test is the measurement of the amount of contaminant that can be recovered from a material using solvent extraction. Extraction efficiency is needed to support any test result that uses solvent-based extractions including: the contact test sampler and remaining- and residual-agent coupon data calculations. The extraction efficiency value is used to correct the test data result such that the reported mass corresponds to the mass of agent in a material (which may be substantially different than the mass of agent extracted from the material). For example, if a solvent has a low extraction efficiency, the resulting test value may appear low compared to a solvent with higher efficiency. Failure to correct for this effect limits the ability to compare test data using different solvents and the ability to accurately calculate the contact hazard.

TOP 8-2-061 identified that the extraction efficiency should be measured, but no guidance for the measurement or use of this value was provided. The SD method contains a method for

determining the extraction efficiency across a range of concentrations from high through requirement encountered at the laboratory scale. The approach is based on a calibration curve to determine the response (e.g., amount extracted) as a function of contaminant concentration. This procedure is conducted for the contact sampler and each material type for each contaminant and extraction solvent. This test is only repeated when significant changes are made to the extraction process and solvent grade or for new material lots. The SD contains the test procedure and detailed data workup using sample data.

3.6 Supporting Analytical (SD Appendix D)

The DTRA-funded project BA06DEC407 was an effort designed to address the challenges associated with quantifying low-level residual agent to support decontaminant contact- and vapor-test evaluations. The program had three main objectives. The primary program objective was to develop improved analytical methods to enable the confident quantitation of low-level of chemical agents VX, HD, and GD at published requirement levels. The lowest requirements at the time of this program used to establish the required detection limits were the Joint Platform Interior Decontamination (JPID) program 2005[4] and Joint Service Sensitive Equipment Decontamination (JSSED) program 2004 requirement documents.[5] The second program objective was to establish methods for the detection of common agent byproducts that could form during decontaminant testing. The third program objective was to make the new methods available to establish uniformity in test procedures across testing locations. The methodology development is documented in a separate report by T. Lalain entitled, "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" (unpublished data, 2009). The formal methods are included in the Appendix.

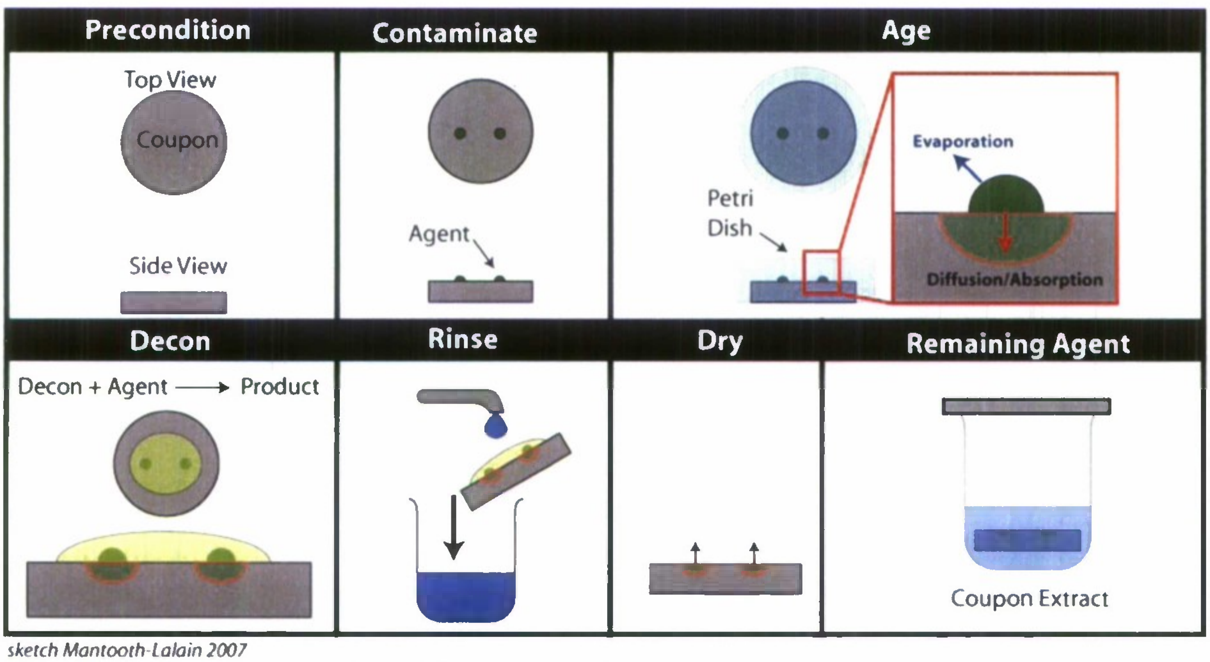

Figure 2. Coupon treatment and remaining agent sampling representation.

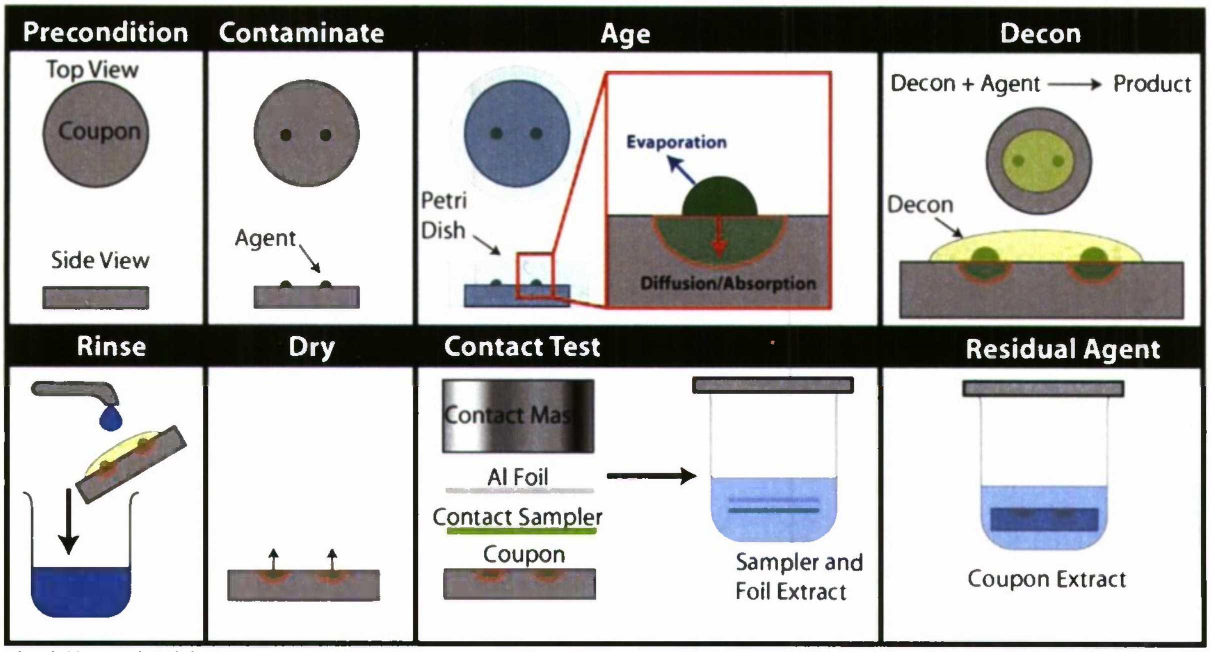

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Figure 3. Coupon treatment and contact sampling representation.

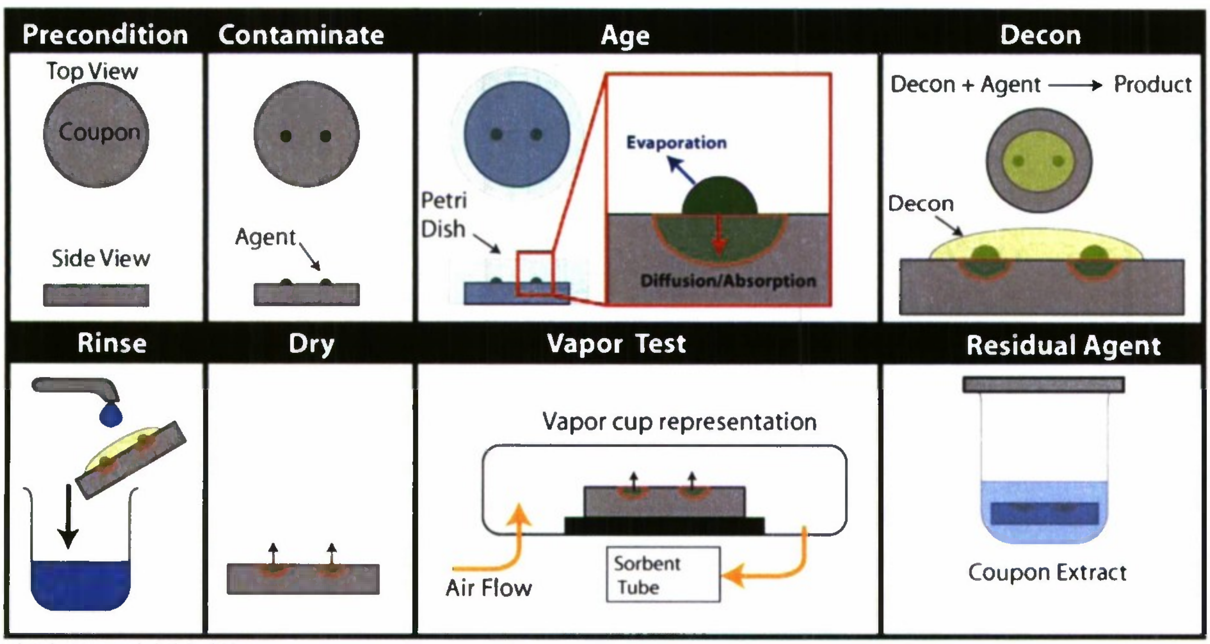

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Figure 4. Coupon treatment and vapor sampling representation.

4. MATERIAL COMPATIBILITY TESTING 2007 UPDATE

The material compatibility tests are used to determine the impact the decontaminant has on the material integrity or the ability to perform the intended function (Figure 5). These tests are typically based on standardized methods and are typically conducted on materials that have not been contaminated because the amount of decontaminant is significantly greater than the amount of contaminant. Many of these tests could be performed on materials that have been contaminated and

decontaminated. Section 5 (SD) does not provide step-by-step procedures for the evaluation of contaminated materials; however, SD method Section 6-A could be used as guide for contamination application, decontamination, and documentation. The metal corrosion, elastomer hardness and sorption, and thermoplastic sorption and transmittance methods were updated as part of another program during FY07. The method updates were included in the FY07 SD for completeness. The 2002 TOP 8-2-061 and FY07 SD do not capture all of the material integrity or compatibility tests that may be of interest to the test sponsor for a given application. Standardized methods should be used when possible. Guidance for the use of standardized test methods for decontaminant evaluations was provided in the FY07 SD.

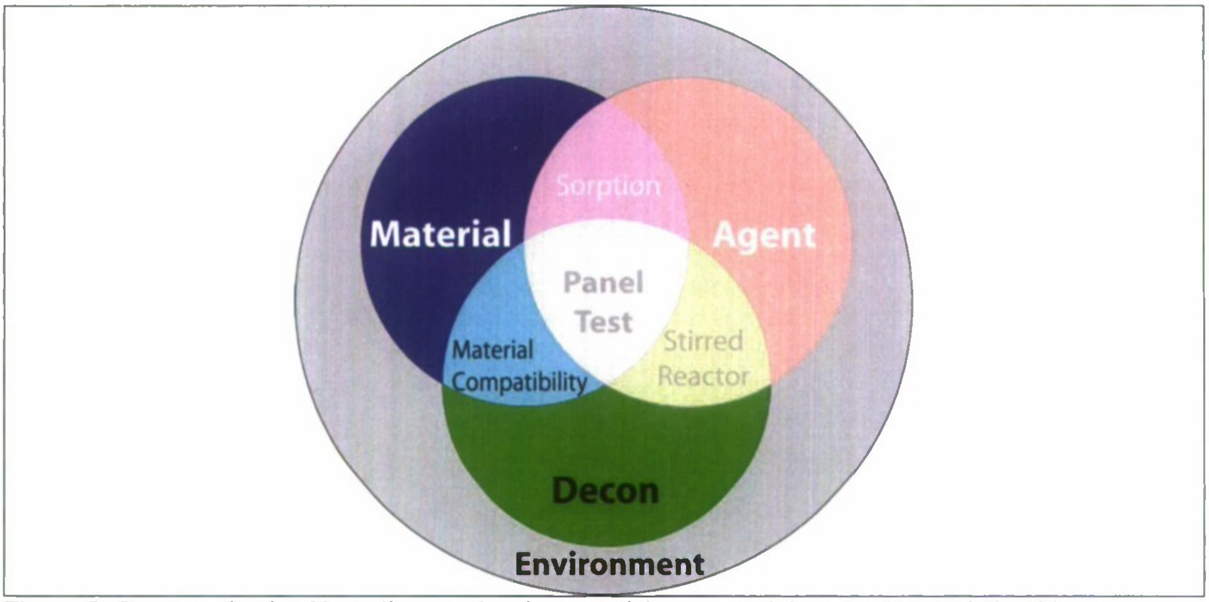

Figure 5. Decontamination Venn diagram showing material, agent, and decontaminant relationships.

4.1 Metal Corrosion Test Method (SD Section 5-A)

Metal corrosion is evaluated using ASTM test method G 31-72 (reapproved 2004) "Standard Practice for Laboratory Immersion Corrosion Testing of Metals."[6] This method describes the accepted procedures for preparing specimens, identifying test apparatus and conditions, cleaning methods, evaluating results, and calculating and reporting corrosion rates. This method identifies these procedures as having influence on laboratory immersion corrosion tests, especially for the determination of mass loss. The mass loss is calculated and reported in milligrams (mg). The corrosion rate is calculated and reported in units of mil-per-year (mpy). Three additional guides for the cleaning, evaluation, and data analysis of corrosion samples are recommended references to evaluate properly and document severely corroded samples.[7-9]

The 2002 TOP 8-2-061 contained an abbreviated method and reporting section for the metal corrosion test method. This method, however, was loosely based on the ASTM method and did not contain the degree of rigor for the test to be executed in accordance with the ASTM standard. The approach for the FY07 SD was to provide sufficient guidance for key test choices and emphasize the need for thorough documentation. The SD requires that all of the required reporting criteria in ASTM G 31-72, Section 12, are addressed in the report. It is understood in chemical decontaminant testing that sometimes test modifications are necessary to meet program objectives. The recommendation is to try to avoid deviating from standardized test methods whenever possible. If deviations are needed, then the report should contain a summary of any changes/modification to the ASTM method made during execution.

The documentation of these deviations is important to capture context that may explain differences in test-to-test or lab-to-lab data.

The evaluation of this method identified several other key considerations for employing this test for decontamination testing. Many of the materials of interest to decontaminant evaluations are corrosion resistant metals used on aircraft and vehicles. Test duration plays a key role in the ability to accurately assess the impact a decontaminant has on the material of interest. The following bulleted list contains some of the guidance for using this method to evaluate decontaminant performance:

- Materials: The standard does note that for some metals, such as titanium and zirconium, the corrosion products are a hard and tightly bonded oxide that cannot be easily removed by standard chemical or mechanical methods. For these cases, the change in mass is reported as a mass gain rather than a mass loss.
- Immersion: Samples can be tested as full immersion, partial immersion, or vapor exposed. The selection is dependent on the test goals; however, the sample must be support vertically. Samples should not rest horizontally in the test apparatus.
- Calibration: The method uses measurement tools such as balance, calipers, and pit gage. These tools should be properly maintained and calibrated an appropriate schedule, typically annually. The use of certified weights to confirm balance operation prior to sample measurements is encouraged.
- Test Duration Guidance:
  - General Guidance: The test duration should not be so long that the specimen size is drastically reduced.
  - Immersion Time and Corrosion Resistant Metal and Alloy Evaluations: The 2002 TOP 8-2-061 specifies a 24 h immersion time. The ASTM standard states that short-time duration tests can give misleading results for metals such as stainless steel. Some metals and alloys form passive films requiring longer immersion times to accurately assess corrosion rates. The ASTM standard provides guidance for selecting the time duration. The standard states the most common testing periods are 48 to 168 h (2 to 7 days). If shorter times are used, the results may be limited to express corrosion only for the length of time studied; data extrapolation might be limited.
  - Planned Interval Test: The ASTM standard provides guidance for test strategies that remove corrosion products between exposure periods. Guidance is provided in the ASTM standard for the proper execution of this test variation.

4.2 Elastomer Sorption and Hardness Test Method (SD Section 5-B)

Elastomer hardness can be determined using ASTM test method D 2240-05 "Standard Test Method for Rubber Property – Durometer Hardness."[10] This method measures the force required to create an indentation in the material. Appropriate materials for this test include thermoplastic elastomers, vulcanized (thermoset) rubber, elastomeric materials, cellular materials, gel-like materials, and some plastics. This test provides a hardness measurement.

The ASTM test method D 471-06 "Standard Test Method for Rubber Property – Effect of Liquids" measures the comparative ability of rubber materials to withstand the effects of liquid contact.[11] Some of the physical characteristics covered by this method include change in mass, volume, dimension, and tensile strength either due to immersion or surface contact. The method is divided into seven subtests.

The guidance for using these tests for decontaminant testing focuses on durometer use and test reporting. The durometer is a specialized measurement tool. Elastomers can be obtained with specification sheets citing hardness. A recommended practice is to conduct a control test to demonstrate

operator and durometer performance on a material of known hardness prior to measuring decontaminant test samples. The guidance for thorough test reporting is provided in the following list:

- All of the required reporting criteria in ASTM D 2240-05, Section 10
  - Note, the reporting instructions emphasize documentation of the durometer calibration status.
- The sections performed from ASTM D 471-06
- The appropriate reporting criteria from ASTM D 471-06, Section 18
- The decontaminant tested including date and time of preparation
- Summary of any changes/modification to the ASTM method made during execution. The documentation of these deviations is important to capture context that may explain differences in lab-to-lab data.
- If related test standards are used, the method should be cited and the method reporting requirements documented.

4.3 Thermoplastic Sorption, Haze, and Transmittance Test Method (SD Section 5-C)

The ASTM test method D 543-06 "Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents" covers the reporting of changes in weight, dimensions, appearance, and strength properties for plastic materials contacted with chemical reagents.[13] ASTM test method D 1003-00 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics" is the evaluation of luminous transmittance and haze.[14] The method contains two procedures for the use of either a hazemeter or spectrophotometer. The haze and transmittance are reported in percent. In decontaminant evaluations, it is desirable to conduct the chemical reagent test and then evaluate for haze and transmittance. Although these methods are written for plastic materials, it is anticipated that they are suitable for glass. These methods may be applicable to other viewport materials. This test is fairly straightforward as modern hazemeters and spectrophotometers are fairly automated.

4.4 Hardness (Coating) Test Method (SD Section 5-D)

The ASTM test method D 3363-05 "Standard Test Method for Film Hardness by Pencil Test" is a simple procedure for determining the film hardness of an organic coating.[15] The method uses a set of calibrated drawing pencils that range in lead hardness. Of the tests documented in this section, this ASTM test method does indicate that this test can produce variable results between laboratories, panels, and operators. The test is best suited within a single laboratory when many of these variables can be strictly controlled. For decontaminant evaluations, the comparison with an untreated material sample provides the data end user with the ability to compare the test result to a control sample. A laboratory should determine within the laboratory the operator repeatability and report that value. The combination of the control data and lab repeatability measurement should assist the data user to assess if variability is due to the coating or operator.

4.5 Guidance for the Use of Standardized Test Methods for Decontaminant Evaluations (SD Section 5-E)

It is anticipated that during decontaminant evaluations, the evaluation of material compatibility for decontaminated and contaminated–decontaminated surfaces may be of interest. In addition, there are many standardized methods that could be employed in decontaminant evaluations based on the material of interest. The ASTM methods presented in this section were those identified in the TOP 8-2-061 initial release. This list is not intended to fully encompass the tests that may be required based on intended acquisition program, final use platform (i.e., vehicles, planes, buildings, equipment, etc.), or program material list.

Quite often in decontaminant literature, thorough documentation of how the method was executed is not provided. This lack of information can create confusion when data are compared over the course of development or between laboratories. Recommendations to facilitate the use of decontaminant data to assess material compatibility include:

- Materials: Provide detailed source and sample preparation details. Whenever possible, obtain vendor specification sheets for stock material used to prepare test samples.
- Contaminants: The documentation should include the contaminants tested, source, lot, and purity.
- Decontaminants: The documentation should include decontaminants tested, source, lot (if available), and date of preparation or expiration date. For R&D evaluations, the decontaminant or applicator model/version number should be noted, as changes in formulation or applicator may require revisiting selected material compatibility tests later in the development program.
- Sample History: The report should include the sample treatment from startup to material compatibility testing for completeness.
- Material Control Tests: A material control test is recommended for most material compatibility tests. This is the evaluation of the test material that has not been treated with contaminant or decontaminant. This test provides a measure of the material integrity for the starting material. In many cases, this value provides a reference for the determination of the degree of material degradation incurred during the treatment process.
- Comparison to Specification Sheets: Specification sheets can be obtained for some materials, especially metals, from the vendor. These specification sheets may contain the minimum requirements per some of the ASTM tests. For example, the tensile strength per ASTM A 240 can be obtained for most metals. If this test is performed in the laboratory and the material control tests do not meet this specification, this is typically an indication that the sample preparation or test was not executed in accordance with the method. If method deviations are clearly documented, it may be suitable to perform the test using the material control as the comparative sample to determine degree of material degradation.
- Process Isolation Tests: For some applications, it may be of interest to evaluate the performance of the decontaminant, applicator, and process (i.e., brushing or scrubbing) independently to determine which process step contributes most to observed material incompatibilities. Process isolation tests are recommended for this case. The process variations should be clearly documented, and the matcrial compatibility test method should not deviate between process isolation evaluations, so the process, not the test method changes, is evaluated.
- Documented Deviations from Test Method: All deviations from the written standard should be documented. It is anticipated that for certain applications, minor modifications may need to be made to achieve test objectives. Documenting that a test was done based on a test method with clearly documented test modifications provides the user of the data the ability to determine data use, context, and comparability.

4.6 pH Measurement (SD Section 3-A)

The measurement of pH was placed within the material compatibility test methods in the 2002 TOP 8-2-061 document. Although this measurement is performed for somc of the ASTM tests, this measurement can be used for most procedures within the SD. The measurcment of pH was relocated to

FY07 SD Section 3-A. The method was updated to include suggested use of standard buffer solutions and measurement practices in accordance with manufacturer's operating instructions.

5. TEST METHODS NOT PENDING UPDATE IN 2006–2007 PROGRAM

This section contains the test methods that were outside the FY06–07 test program scope and were not updated. To ensure that no chemical decontaminant testing information was lost, the 2007 SD contains the procedures from the 2002 TOP 8-2-061. The FY07 SD objectives were as follows:

- Capture the procedure from 2002 TOP so that all tests are accounted for in the 2007 SD
- Reorganize tests by common theme
- Align with SD format such that each section is a stand alone unit with all required tests required to complete the test (i.e., analytical)
- Provide guidance to improve test documentation.

The methods are included in the SD for completeness and reformatted to align with the SD format. The FY08 program, as proposed at the time of this report, anticipates addressing the updating of the test planning section, stirred reactor test method, and method development for the evaluation of decontaminant process rinse water for which placeholder sections were added to the 2007 SD.

5.1 Chemical Kinetics Determination via Stirred Reactor Test (SD Section 4)

The stirred reactor test is the evaluation of a decontaminant to neutralize agent under ideal conditions in that there are no material affects impacting decontaminant performance (Figure 6). This test is routinely used to evaluate decontaminant performance early in the decontaminant development timeline to measure reaction kinetics or endpoint.

The update of this test method has been proposed for the FY08 program. The anticipated updates include documented guidance regarding the use of the test for chemical kinetics versus endpoint determination. Although the procedure can be used for both tests, kinetics versus endpoint utilize different portions of the data curve (Figure 7). The chemical reaction kinetics (i.e., decontaminant-agent chemistry) is a core component to understanding the decontamination process and how decontaminants and their ingredients affect the reaction chemistry. Sufficient data points are needed to evaluate the reaction curve to determine the kinetics. Similarly, sufficient points are needed to establish an endpoint. Also, the test will be evaluated to address the data scatter observed for agents that are not miscible with aqueous-based decontaminants that could give a false negative that the endpoint was achieved. Similar to the FY07 SD, the procedures will include necessary calculations and data interpretation and utilization guidance.

5.2 Test Planning and Design (SD Section 2)

The test planning section is anticipated to be developed as part of the FY08 program. This section will focus on setting objectives and selecting the appropriate tests to meet the stated objectives. This section will emphasize the need for documentation rigor to enable test data utilization in appropriate context and traceability of test results. This section will include test selection and data utilization guidance to benefit data users such as test directors, program managers, and testing staff.

5.3 Rinsate Analysis (SD Sections 6-C and 7-B)

Physical removal can be effective at reducing the amount of contaminant present on the surface of interest. Physical removal alone does not necessarily neutralize a decontaminant. The contaminant is simply relocated from one area to another. Decontaminant testing is traditionally focused

on the surface of interest. This context of relocating the hazard becomes important in situations where the secondary hazard is of equal importance as the original hazard. Examples include cross contamination to other assets, runways, ship decks, and domestic scenarios where the ability to remain in the original area is necessary. The complete evaluation of a reactive decontaminant should include the evaluation of rinse water to confirm contaminant neutralization. The original TOP does indicate that this sample should be collected and analyzed; however, the original document does not specify how to conduct this analysis, use the data, or how to address analysis challenges such as matrix effects when evaluating complex mixtures such as rinsate. This section was added to the SD and has been proposed for the FY08 updates.

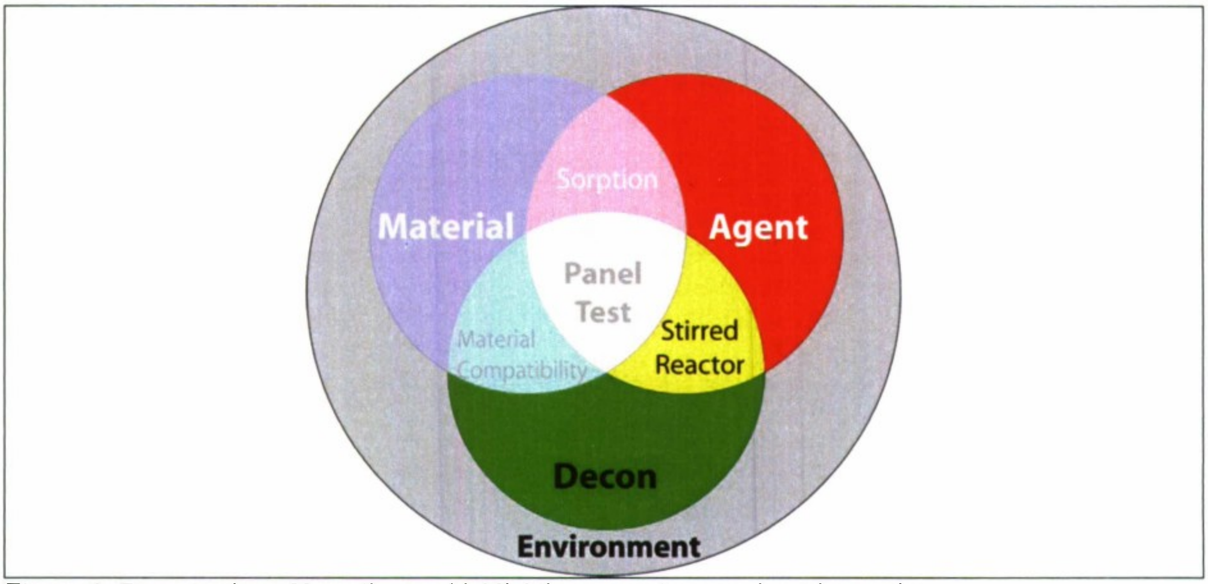

Figure 6. Decontaminant Venn diagram highlighting agent-decontaminant interaction.

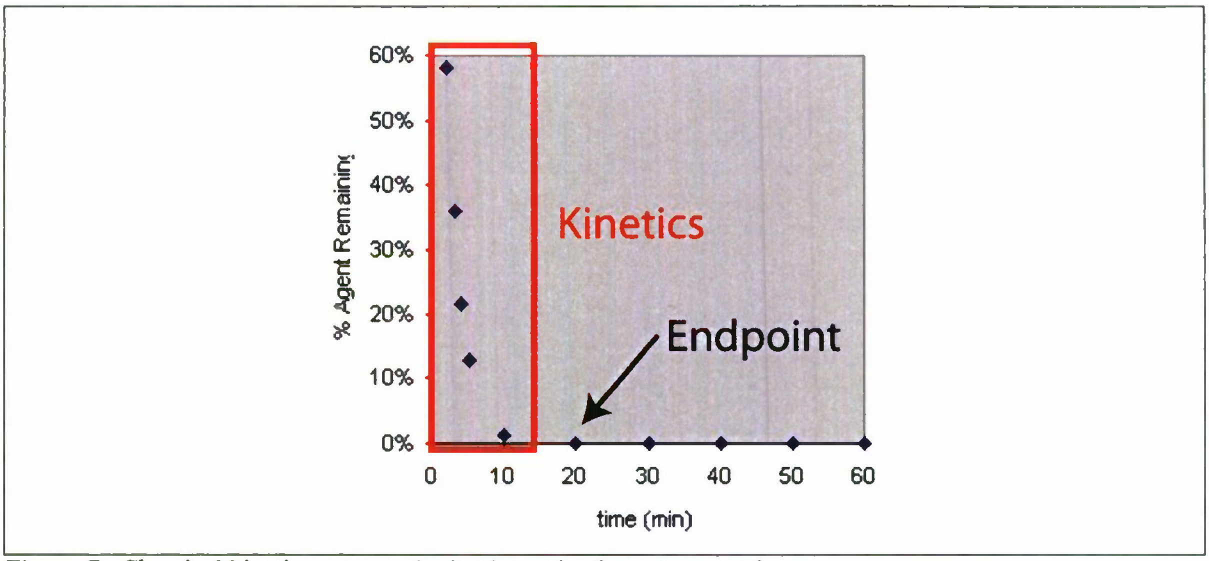

Figure 7. Chemical kinetic versus endpoint determination representation.

5.4 Detection and Protection Methods (SD Section 8)

The FY07 SD Section 8 contains the test methods for Convective Flow for Air Permeable Materials, Detector Compatibility Test with Decontaminant, and Individual Protective Equipment and Collective Protective Equipment Compatibility.

Convective Flow for Air Permeable Materials Test Method: According to the 2002 TOP 8-2-061, "the objective of this live-agent test is to measure the ability of an air-permeable material to resist convective penetration of a chemical agent after the material had been contaminated with a decontamination solution." The test method is based on TOP 8-2-501 "Permeation and Penetration Testing of Air-Permeable, Semi-Permeable Materials with Chemical Agents or Simulants (Swatch Testing)" dated 3 March 1997. No new analytical data were generated in order to evaluate the test procedure performance to determine if updates are required. Recommended updates to test reporting were added to the procedure. The additional recording and reporting requirements added to the test method are shown in underlined, italicized text.

Detector Compatibility Test with Decontaminant Test Method: According to the 2002 TOP 8-2-061, "this test procedure is for the determination of the impact a de contaminant has on the ability of a detector to perform in the presence of decontaminant." No new analytical data were generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional recording and reporting requirements added to the test method are shown in underlined, italicized text.

Individual Protective Equipment and Collective Protective Equipment Compatibility Test Method: According to the 2002 TOP 8-2-061, "this test determines the effects of decontaminant exposure on individual and collective protection systems hardware. This test is designed to measure any degradation caused by the decontaminant on selective aspects of the system's performance from that of the baseline performance established in the Individual Protective Equipment (IPE) and Collective Protective Equipment (CPE) product performance specifications." The test method is based on TOP 8-2-501 "Permeation and Penetration Testing of Air-Permeable, Semi-Permeable Materials with Chemical Agents or Simulants (Swatch Testing)" dated 3 March 1997. No new analytical data were generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method are shown in underlined, italicized text.

5.5 Decontaminant Pot- and Shelf-Life Methods (SD Section 3)

Section 4 (FY07 SD) contains the test methods for decontaminant pot and shelf life.

Laboratory Test – Pot Life: According to the 2002 TOP 8-2-061, "this test determines the useful life characteristics of the decontaminant under normal use conditions. This test is designed to measure any degradation in critical performance parameters from that of the product's baseline performance resulting from changes in the products physical state or chemical composition during a typical mission period." No new analytical data were generated in order to evaluate the test procedure performance to determine if updates are required. Many of the TOP 8-2-061 2002 release methods used the phrase "or as otherwise specified." The purpose for this phrasing was to enable test directors flexibility during test execution. In some cases, though, this flexibility impacts the ability to compare data sets from test to test or lab to lab, especially if the deviation is not well documented. Because deviations to the test method can limit the ability to compare decontaminants impacting the ability to compare new and emerging decontaminants to standard/fielded decontaminants, the documentation requirements were added to the text to require the documentation of all pertinent information during

testing. This recommended strengthening of the test procedure and reporting updates was added to the procedure and identified by the use of italicized, underlined text.

Laboratory Test –Shelf Life/Accelerated Aging: According to the 2002 TOP 8-2-061, "this test determines the storage/shelf life characteristics of the decontaminant under normal storage conditions by thermally inducing accelerated aging of the product. This test is designed to measure any degradation caused by the accelerated aging on selective aspects of the decontaminant's performance from that of the product's baseline performance established by Government or contractor test data or product specifications." No new analytical data were generated in order to evaluate the test procedure performance to determine if updates are required. Similar to the Pot Life test, this test procedure contains non-specific requirements to enable test directors flexibility during test execution. The test does not specify the three test temperatures, which places the responsibility on the test sponsor to ensure that the selected conditions are realistic or in accordance with applicable requirement documents. In addition, the method does not reference the source of the procedure cited. This recommended strengthening of the test procedure and reporting updates was added to the procedure and identified by the use of italicized, underlined text.

LITERATURE CITED

1. *Field Manual 3-11.5: CBRN Decontamination: Multiservice Tactics, Techniques, and Procedures for Chemical, Biological, Radiological, and Nuclear Decontamination*; April 2006.

2. *Field Manual 3-11.9: Potential Military Chemical/Biological Agents and Compounds*; FM 3-11.9; 2005.

3. *CHEMICAL AND BIOLOGICAL DECONTAMINANT TESTING*; TOP 8-2-061 (Initial Release); U.S. Army Developmental Test Command, (CSTE-DTC-TT-S): Aberdeen Proving Ground, MD, 19 November 2002.

4. *Operational Requirements Document (ORD) for Joint Platform Interior Decontamination (JPID) (V1.4)*; JROC: Washington D.C., Updated May 2005.

5. *Operational Requirements Document (ORD) for Joint Service Sensitive Equipment Decontamination (JSSED)*; JROC: March 2004.

6. *Standard Practice for Laboratory Immersion Corrosion Testing of Metals*; G 31 - 72 (Reapproved 2004); ASTM International: West Conshohocken, PA.

7. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*; G 1 – 03; ASTM International: West Conshohocken, PA, 1 October 2003.

8. *Standard Guide for Applying Statistics to Analysis of Corrosion Data*; G 16 – 95 (Reapproved 2004); ASTM International: West Conshohocken, PA, 1 May 2004.

9. *Standard Guide for Examination and Evaluation of Pitting Corrosion*; G 46 – 94 (Reapproved 2005); ASTM International: West Conshohocken, PA, 1 May 2005.

10. *Standard Test Method for Rubber Property—Durometer Hardness*; D 2240 – 05; ASTM International: West Conshohocken, PA, 15 August 2005.

11. *Standard Test Method for Rubber Property—Effect of Liquids*; D 471 – 06; ASTM International: West Conshohocken, PA, 15 November 2006.

12. Iverson, S.; Thomas, H.; Weatherhead, D. C. J.; Ferguson, K. *Data Comparison Report for the Decontamination Chamber and Decon Green Efficacy Tests*; WDTC-DR-05-138; West Desert Test Center, Dugway Proving Ground: Dugway, UT, February, 2006. UNCLASSIFIED Report

13. *Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents*; D 543 – 06; ASTM International: West Conshohocken, 1 April 2006.

14. *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics*; D 1003 – 00; American Society for Testing and Materials: West Conshohocken, PA, 10 June 2000.

15. *Standard Test Method for Film Hardness by Pencil Test*; D 3363 – 05; ASTM International, West Conshohocken, PA, 1 January 2005.

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ACRONYMS

APG	Aberdeen Proving Grounds
ASTM	The American Society for Testing and Materials
BPR	Business Process Reengineering
CARC	Chemical Agent Resistant Coating
CBRN	Chemical, Biological, Radiological, and Nuclear
CCV	Continuing Calibration Verification
CONOPS	Concept of Operations
DoD	Department of Defense
DT/OT	Developmental and Operational Testing
DTRA	Defense Threat Reduction Agency
ECBC	Edgewood Chemical Biological Center
ISO	International Standards Organization
JMDS	Joint Materiel Decontamination System
JPEO-CBD	Joint Program Executive Office for Chemical Biological Defense
JPID	Joint Platform Interior Decontamination
JSSED	Joint Service Sensitive Equipment Decontamination
JSTDS-LS	Joint Tactical Decontamination System – Large Scale
JSTO	Joint Science and Technology Office
KPP	Key Performance Parameter
MOPP	Mission Oriented Protective Posture
mpy	mil-per-year
ORD	Operations Requirement Document
PI	Principal Investigator
QA	Quality Assurance
QC	Quality Control
R&D	Research and Development
S&T	Science and Technology
SD	Source Document
T&E	Testing and Evaluation
TOP	Test Operations Procedure
TRA	Technology Readiness Assessment
TRL	Technology Readiness Level

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APPENDIX

2007 SOURCE DOCUMENT

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APPENDIX

2007 Source Document
Chemical Decontaminant Performance Evaluation Testing

Planning, Test Procedures, and Reporting Requirements for Routine Chemical Decontaminant Tests Used to Evaluate Decontaminant Performance

Source Document to Support the Update of TOP 8-2-061 Existing Methods

Prepared By: Decontamination Sciences Team
Edgewood Chemical Biological Center
Research & Technology Directorate

Project Title: Improved Test Methods
Project Number: BA06DEC414
Decontamination Sciences Portion

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Section 1: Introduction

If contamination occurs, there is the need to reduce the risk to personnel and equipment while maintaining the ability to complete the mission. There are four levels of decontamination: immediate, operational, thorough, and clearance.[1] Each level has specific objectives and specifications for the reduction of contamination. Immediate decontamination occurs within 15 minutes of contamination with an emphasis on saving lives and limiting contamination spread. Operational decontamination is performed to sustain operations by reducing the spread of contamination and providing temporary relief from long-term mission oriented protective posture (MOPP). FM 3-11.5 recommends that operational decontamination be initiated within 1 hour for chemical agent resistant coating (CARC) coated surfaces and within 6 hours for non-CARC surfaces. Thorough decontamination is the significant reduction in contamination level for long-term MOPP reduction. Thorough decontamination is initiated when the mission allows; however, the field manual does recommend an initiation time as short as possible as many decontamination techniques become less effective over time. Clearance decontamination is the reduction in contamination to a level that allows for unrestricted use, transportation or disposal. In order to support field needs, decontaminants are evaluated through a development and testing process.

Decontaminant development and testing typically focuses on thorough decontamination identifying decontaminants that can significantly reduce contamination in a short period of time that are safe to personnel and equipment. In the decontamination business area (now called hazard mitigation), all emerging decontaminants and technologies are required to demonstrate the ability to meet a specified set of key performance parameters (KPPs) per the acquisition program Operational Requirement Document (ORD). One of the specific KPPs to be demonstrated is that of chemical agent decontamination efficacy. The chemical agent efficacy determination is accomplished through the execution of the standard panel contact- and vapor-tests as documented in Test Operations Procedure (TOP) 8-2-061. At the research and development (R&D) 6.2 and 6.3 stages, these tests provide the data set that is evaluated during transition activities such as the Technology Readiness Assessment (TRA) to determine the technology readiness level (TRL) and to support Milestone A and B decisions. Similarly, DT/OT testing utilizes these same test procedures post milestone B for TRLs 7 through 9.

The data generated from the S&T and DT/OT testing must be defensible and comparable in order to identify the next generation technologies and support acquisition transition tasks such as TRAs, milestone reviews, and third party data evaluations. Historical test documentation is often of limited value due to lack of thorough documentation regarding test design, execution, and quality control (i.e., testing conditions, use of control tests, analytical CCV samples, and data acceptance procedures). The comparison of decontaminant test data from different laboratories or for different technologies has been limited to approximations as the current test protocols are not detailed enough and the documentation requirements are limited preventing the ability to easily compare data and provide the full context of the test conditions. The inability to compare data creates management challenges for the selection of the best decontaminant technology for an acquisition program. The lack of specific methods and data utilization limitations often results in the need for additional testing.

The past approaches for decontaminant technology development and testing are further challenged by the lack of data calculation methodologies. As a result, different test facilities may perform data calculations in different ways to determine if a technology meets a requirement such as a contact or vapor hazard. The method and calculation vagueness creates

a range of results from technologies that may perform well in some aspects, but may overlook advantages, limitations, or caveats in the data. As the need for product development on shortened time schedules and reduced funding increases, there is a need to collect accurate data that can be compared to requirements and other decontaminants to support management reviews. The methodology should be rigorous to enable data comparisons with enough flexibility to enable testing at different conditions, stages, and with different technologies. The combination of rigor and flexibility is enabled through thorough documentation of what was tested, how it was tested, and uniform treatment of the data to provide the necessary context required to properly interpret the data. The need for additional testing can be minimized by identifying the objectives of the acquisition program and performing the tests that address the needs and KPPs of the program.

DTRA JSTO program BA06DEC414 is the foundation toward change by first improving the test structure which is used to perform the Decon mission. DTRA program BA06DEC414 was initiated in FY06 to update these methods. The primary objective was to improve the rigor of existing test methods for the contact- and vapor-test from TOP 8-2-061[3] "Chemical Biological Decontaminant Testing" for the generation of defensible and comparable decontamination efficacy data for the quantitative determination of post-decontamination contact- and vapor-hazards and residual agent. Execution of these improved methods will yield higher fidelity data presented in an appropriate context. The data generated from these updated methods enhances all components of the decontaminant lifecycle including research and development (R&D), science and technology (S&T), testing and evaluation (T&E), and developmental and operational testing (DT/OT) activities, technology readiness assessments (TRA) to determine technology readiness level (TRL), technology comparisons, risk assessments and milestone decisions. This program has utilized practices from Business Process Reengineering and recognized international standards (e.g., ASTM, ISO) during the effort. Business Process Reengineering (BPR) is a management approach aiming at improvements by means of elevating efficiency and effectiveness of the processes under investigation. These tools are applied to this program by systematically evaluating the test processes and identifying the variables that have the greatest impact on the test results; more specifically, by determining the resulting post-decontamination hazard. The format used to document the test method improvements was designed to ensure that all of the necessary elements were captured.

The Chemical Decontaminant Performance Evaluation Source Document (SD) was a product from this program. The Source Document format uses a blend of scientific text book educational format and required ASTM and ISO fields. The scientific text book approach informs the reader regarding the test purpose, test limitations, and other associated tests so that the proper tests can be selected based on program objectives. For example, decontamination methods include neutralization, physical removal and weathering. Neutralization is the reaction of the contaminant and the decontaminant material to produce a reaction product that is of lower-toxicity compared to the original contaminant. Physical removal is the relocation of the contamination from the surface of interest to a surface of lesser importance. Weathering includes processes such as evaporation. The source document provides guidance on which test to execute and specifies how to calculate each of these values. Most decontaminants and decontamination processes use a combination of neutralization and physical removal. If a decontamination process used a pre-rinse process in addition to the decontaminant treatment, some of the contamination may be physically removed. If the program objective was to achieve a high degree of chemical neutralization, then the rinse water must be collected and analyzed to determine the amount of contaminant that was relocated. Failure to collect and analyze the rinsate could give a false confidence that a high degree of neutralization occurred. The Source Document contains detailed data calculation methods. Each test also includes acceptance

criteria and discusses the impact of the major system variables. The text book style is used to demonstrate specific calculation methods using small sets of data. The use of ASTM and ISO fields enable performing laboratories to introduce these methods into their quality systems.

The Source Document contains a test planning chapter, six test method chapters and associated appendices. A general description of each chapter is provided in the bulleted list.

- **Section 2: Test Planning.** The test planning section is anticipated to be developed in the FY08 program. This section will focus on setting objectives and selecting the appropriate tests to meet the stated objectives. The section will include test selection and data utilization guidance to benefit test directors, program managers, and other data users.
- **Section 3: Decontaminant Preparation and Evaluation.** This section contains the test methods for measuring decontaminant pH, Pot-Life, and Shelf-Life / Accelerated aging.
- **Section 4: Chemical Kinetics Determination via Stirred Reactor Test.** The stirred reactor test is the evaluation of a decontaminant to neutralize agent under ideal conditions in that there are no material effects impacting decontaminant performance. The test is typically conducted for new decontaminant formulations compared to a reference decontaminant, typically household bleach.
- **Section 5: Material Compatibility Testing.** The material compatibility tests are used to determine the impact the decontaminant has on the intended material function. These tests are typically conducted materials that have not been contaminated with agent. These tests could be performed on materials that have been contaminated and decontaminated.
- **Section 6: Panel Test to Determine Contact Hazard.** The contact test series contains the procedures for the measurement of contaminant present after the decontamination process that could pose a hazard to unprotect personnel through skin or contact transfer to other surfaces. These tests utilize a contact sampler as a surrogate for human skin, coupons of operationally relevant surfaces of interest, solvent extraction, and chromatographic analytical methods. The rigorous laboratory-scale test method uses a standard two inch diameter circular coupon. The methods can be applied to larger coupons and test articles. These tests can be used to evaluate decontaminants in liquid-, solid-, or vapor-form.
- **Section 7: Panel Test to Determine Vapor Hazard.** The vapor test series contains the procedures for the measurement of contaminant vapor present after the decontamination process that could pose a vapor hazard to unprotected personnel. These tests utilize a vapor chamber to capture contaminant vapor emissions from the material to calculate an emission factor which is then used to determine the vapor-hazard for the scenario. The rigorous laboratory-scale test method uses a standard a two inch diameter circular coupon. The FY08 update will include methods for the evaluation of larger coupons and test articles. These tests can be used to evaluate decontaminants in liquid-, solid-, or vapor-form.
- **Section 8: Detection and Protection Test Methods.** This section contains the test methods for Convective Flow for Air Permeable Materials, Detector Compatibility Test with Decontaminant, and Individual Protective Equipment and Collective Protective Equipment Compatibility.
- **Appendix A: Acronym and Abbreviation List.** The acronyms and abbreviations used throughout this document for chemical decontaminant testing protocols are listed in this Appendix. The acronyms and abbreviations are divided based on general categories. Laboratories using these methods should avoid using acronyms

that overlap with document specific acronyms. All laboratory specific acronyms used in test documentation not listed in this Appendix should be defined in the test plan and defined on first usage.

- **Appendix B: Suggested Material and Contaminant List.** This appendix contains information regarding coupon materials, contaminants, and decontaminants.
- **Appendix C: Low-Level Analytical Methods.** This appendix contains the methodology developed under program CA06DEC407 regarding the analytical methods to detect and quantify the contaminants (i.e., agent).

The 2007 Chemical Decontaminant Performance Evaluation Source Document contains the updated contact- and vapor-test methodology. The contact test chapter includes specific test methodology for determining the remaining agent and performing the contact test, including supporting methods for extraction efficiency determinations and chromatographic analysis. The test procedures contain options allowing for test modifications and guidance on how those modifications may impact data calculations. The contact test chapter contains detailed data calculations for determining percent efficacy, percent neutralization, and contact hazard. The calculations are further divided into calculated, approximated, or inferred calculations. These divisions are based on the availability of required data and indicate the degree of rigor used to calculate the result.

The vapor hazard test underwent the most significant improvement. The method for calculating vapor hazard was historically based on the vapor concentrations directly measured in the vapor chamber. The result is often an overestimation of the hazard. Overestimating the resulting hazard can impact decontamination development resulting in greater logistical requirements and increased potential for material incompatibilities. In addition, the comparison of chamber vapor concentration to a requirement to determine if a toxicological response will occur was not correct. The documented methods are now aligned with the DoD accepted method for the determination of a vapor exposure using a toxic load calculation.[2] This calculation does require the specification of a scenario for complete analysis. This new calculation method is demonstrated using a small set of sample data and six example scenarios.

For completeness, the Source Document also contains relevant methodology improvements from other programs and the other TOP 8-2-061 tests not updated as part of this program. The low-level analytical methodology developed under program CA06DEC407 is included. The TOP 8-2-061 methods not updated during the FY06-07 program include the chemical kinetics determination via stirred reactor test, convective flow for air permeable materials test, detector compatibility test with decontaminant, individual protective equipment and collective protective equipment compatibility tests. These Source Document sections contain the procedures directly from TOP 8-2-061 (2002 release). In addition, suggestions are provided for both test preparation and documentation since no new data was collected to evaluate the test procedure.

CA07DEC499 is an extension of the methodology program aimed at establishing contact and vapor testing for small items of sensitive equipment. These methods have direct application to upcoming DT/OT testing for the Joint Materiel Decontamination System (JMDS) acquisition program and the Joint Tactical Decontamination System – Large Scale (JSTDS-LS) programs of record.

REFERENCES

1. ARMY *Field Manual 3-11.5: CBRN Decontamination: Multiservice Tactics, Techniques, and Procedures for Chemical, Biological, Radiological, and Nuclear Decontamination*; April, 2006.
2. ARMY *Field Manual 3-11.9: Potential Military Chemical/Biological Agents and Compounds*; FM 3-11.9; 2005.
3. *CHEMICAL AND BIOLOGICAL DECONTAMINANT TESTING*; TOP 8-2-061 (Initial Release); U.S. Army Developmental Test Command, (CSTE-DTC-TT-S): 314 Longs Corner Road, Aberdeen Proving Ground, MD 21005-5055, 19 November, 2002.

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Section 2: Test Planning, Considerations, and Requirements

DESCRIPTION

The test planning, considerations and requirements section walks through the items that must be considered for the execution of the test procedures in this document. These considerations and requirements range from safety and security requirements to specific test needs such as materials and equipment. In addition, this section emphasizes the identification of the test objectives to enable selection of the correct test procedures to meet the objectives.

TABLE OF CONTENTS

This chapter is anticipated to be part of the FY08 release.

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Section 3: Decontaminant Preparation and Properties

DESCRIPTION
This section contains the decontaminant preparation and evaluation test procedures documented in TOP 8-2-061 (Initial Release) dated November 19, 2002 that were not updated as part of the FY06-07 test program. The methods were reviewed during this effort and recommended reporting additions provided.

CONTENTS
3A - Measurement of Decontaminant pH

3B - Laboratory Test – Pot Life*

3C - Laboratory Test –Shelf Life/Accelerated Aging*

NOTES
*Method not updated as part of FY06-FY07 effort.

Test Procedure 3-A: Measurement of Decontaminant pH

SUMMARY OF PROCEDURE

The purpose of this test is to measure the pH of the decontaminant. This test is typically conducted before the decontaminant is used. However, there are a few other tests which use pH measurements. The pH measurement before and after stirred reactor testing can be conducted. Several of the material compatibility tests also have procedures using this measurement. This test provides a measure of pH.

TERMINOLOGY

Terminology specific to this test method include:

- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **pH:** a measure of the acidity or alkalinity of a solution.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- Buffer solutions
- Distilled / Deionized water
- Decontaminant solutions

EQUIPMENT

- pH Meter

MATERIALS

- **Containers**: Appropriate containers for decontaminant solution, buffer solutions and rinse water waste.
- **Standard Laboratory Record Keeping Items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **General Laboratory Items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper toweling, beakers, vials, spatulas, parafilm, etc.

ADDITIONAL SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

1.1 Check that the pH meter is operational and calibrated by measuring the pH of a buffer solution. pH meter calibration should be checked at the beginning of each test day used.

1.2 Follow the manufacturer operation instructions for use and cleaning probe between solutions.

1.3 Select appropriate buffer standard according to table below. Record the pH reading on the datasheet or laboratory notebook. Buffer readings should be within 5% (vendor versus practice) of standard value. If not, recalibrate the instrument as specified in manufacturer instructions and re-measure the buffer solution(s).

Expected Decontaminant pH	Appropriate Buffer Standard
$0 \leq pH \leq 6$	4.0
$6 \leq pH \leq 8$	7.0
$8 \leq pH \leq 12$	10.0

1.4 Consult the vendor operation manual for frequency of calibration checks during use. In general, the calibration should be checked/corrected for drift every 2 hours, or prior to each measurement session on a given test day.

1.5 Evaluate decontaminant solutions

TEST REPORTING

Record on the data test form or appropriate laboratory notebook

- The buffer standard(s) used and expiration date(s)
- Time and date of standard measurement
- Measured pH values for standards and decontaminant solutions evaluated
- Test location temperature and relative humidity

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Data acceptance criteria: Buffer solution standard pH measurements should be within either 5% of standard value or manufacturer specifications.

Corrective Action: recalibrate instrument

CALCULATIONS

None.

REVISION HISTORY

March 2008: original document in source document format. Based on TOP 8-2-061, 2002 initial release. Text was updated to suggested standard buffer solutions and measurement practices.

Test Procedure 3-B: Laboratory Test – Pot Life

SUMMARY OF PROCEDURE

According to the 2002 TOP 8-2-061, "this test determines the useful life characteristics of the decontaminant under normal use conditions. This test is designed to measure any degradation in critical performance parameters from that of the product's baseline performance resulting from changes in the products physical state or chemical composition during a typical mission period."

TERMINOLOGY

No specific terms defined for this test in TOP 8-2-061 (Initial Release) dated Nov. 19, 2002.

REFERENCED DOCUMENTS

No specific references cited for this test in TOP 8-2-061 dated Nov. 19, 2002.

REAGENTS, MATERIALS AND EQUIPMENT

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

General

(1) This test determines the useful life characteristics of the decontaminant under normal use conditions. This test is designed to measure any degradation in critical performance parameters from that of the product's baseline performance resulting from changes in the products physical state or chemical composition during a typical mission period. The test duration shall be 12 hr, **or as otherwise specified by the test sponsor**. *If a time other than 12 hours is used, the test director should note in the test report:*

- *The total time duration used during testing*
- *The rationale / justification for using a time other than that specified in the procedure*

(2) The test shall be conducted at low [~-32 °C (~-25 °F)], ambient [21°C (~70 °F)], and high [~49 °C (~120 °F)] temperatures, and at low (< 20%) and high (> 90%) RH, **or as otherwise specified by the test sponsor**.

Procedure

(1) Duplicate samples of the decontaminant will be obtained in the original unopened containers. The decontaminant samples will be prepared IAW standard procedures for field use of the product.

(2) One of the decontaminant samples will be evaluated at the specified test conditions for the critical performance characteristics specified by the test sponsor.

(3) Performance evaluations of the decontaminant samples will be repeated at 4 hr, 8 hr, 10 hr, and 12 hr, **or as otherwise specified by the test sponsor**. *If times other than 4-, 8-, 10 and 12-hours are used, the test director should note in the test report:*

- *The specific performance evaluation test intervals used*
- *The rationale / justification for using a time interval other than that specified in the procedure*

TEST REPORTING

The following data will be reported:

(a) *Test conditions including*

- *The total time duration used during testing including the rationale / justification for using a time other than that specified in the procedure.*
- *The specific temperature and relative humidity pairs evaluated including.*
  - *Starting temperature and relative humidity*
  - *End temperature and relative humidity*
  - *Highest and lowest temperature and relative humidity observed during the testing.*
  - *If electronic data logging of temperature and relative humidity is available, the report should include the average temperature and range and average relative humidity and range during testing. Charts of electronically logged conditions are encouraged in final test reports.*
- *Specific test intervals used including rationale / justification for using a time interval other than that specified in the procedure.*

(b) Decontaminant: type, quantity, concentration *and date of preparation*.

(c) Performance characteristic measurements.

(d) Estimated decontaminant pot life *in units of hour*

(e) All deviations from the test procedure are documented and reason for deviation provided.

(f) Specific change and rationale for all steps using parameters falling under "or as otherwise specified by the test sponsor."

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

REVISION HISTORY

March 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method and are shown in underlined, italicized text.

Test Procedure 3-C: Laboratory Test –Shelf Life/Accelerated Aging

SUMMARY OF PROCEDURE

According to the 2002 TOP 8-2-061, "this test determines the storage/shelf life characteristics of the decontaminant under normal storage conditions by thermally inducing accelerated aging of the product. This test is designed to measure any degradation caused by the accelerated aging on selective aspects of the decontaminant's performance from that of the product's baseline performance established by Government or contractor test data or product specifications."

TERMINOLOGY

No specific terms defined for this test in TOP 8-2-061 (Initial Release) dated Nov. 19, 2002.

REFERENCED DOCUMENTS

No specific references cited for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002.

REAGENTS, MATERIALS AND EQUIPMENT

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

General

(1) This test determines the storage/shelf life characteristics of the decontaminant under normal storage conditions by thermally inducing accelerated aging of the product. This test is designed to measure any degradation caused by the accelerated aging on selective aspects of the decontaminant's performance from that of the product's baseline performance established by Government or contractor test data or product specifications.

(2) Before the start of the accelerated aging test, product properties or performance characteristics to be used to evaluate the decontaminant will be identified. A quantitative measure of the quality of the decontaminant is to be determined based on these characteristics with a nominal value of 100 when the product is initially produced. This quantitative measure will decrease as the product ages. Products with quantitative measures less than a predetermined threshold for the product shall be considered out of compliance.

Procedure

(1) Duplicate samples of the decontaminant in the original unopened containers will be obtained. One of the samples will be evaluated at a nominal ambient storage temperature of 25 °C (77 °F), for the characteristics specified by the test sponsor.

(2) Fifteen test samples of the decontaminant will be transferred into clean, non-reactive, thermally stable, hermetically sealable containers; the containers will be tightly closed. The original product containers may be used for this purpose, if deemed suitable. Each test sample container should contain sufficient product to perform all characterization testing prescribed herein.

(3) Five test samples will be placed in each of three test temperature environments selected on the basis of an evaluation of the products physical composition **or as specified by the test sponsor**. The selected environmental conditions should not, however, result in unrealistic failure modes that could never occur under real-time ambient conditions. Humidity conditions should be constant, at less than 20 percent RH, **or as otherwise specified by the test sponsor**.

(4) Over a period of 5 months, a product sample should be withdrawn from the test containers monthly, and the quantitative measure of the decontaminant should be determined and recorded.

TEST REPORTING

The following data will be reported:

(a) Test conditions:

- *Test temperatures: the three test temperature environments must be clearly identified and documented in Procedure step (5a). In addition, the justification for each temperature environment should be documented. The justification and environment must be reviewed by both the test director and sponsor to ensure that the conditions are realistic.*
- *The specific relative humidity tested. If a relative humidity other than <20 % RH is used, the test director should note in the test report:*
    - *The specific relative humidity used*
    - *The rationale / justification for using a relative humidity condition other than that specified in the procedure*
- *Detailed temperature and relative humidity monitoring during the test interval*
        - *Starting temperature and relative humidity*
        - *End temperature and relative humidity*
        - *Highest and lowest temperature and relative humidity observed during the testing.*
        - *If electronic data logging of temperature and relative humidity is available, the report should include the average temperature and range and average relative humidity and range during testing. Charts of electronically logged conditions are encouraged in final test reports.*
    - *Specific test intervals used including rationale / justification for using a time interval other than that specified in the procedure.*
- *Date and time for start of test, regular sampling and end of test.*

(b) Type, quantity, and concentration of decontaminant. For multi-component decontaminants, the corresponding values for all components should be recorded.

(c) Performance characteristics used to calculate the products quantitative measure of quality.

(d) Quantitative measurement values for each sample collected during the test period.

(e) Estimated product shelf-life based on analysis of test data *in units of days/months*

(f) All deviations from the test procedure are documented and reason for deviation provided.

(g) the decontaminant original quantitative results for comparison to the aging results.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

REVISION HISTORY

March 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method and are shown in underlined, italicized text.

Section 4: Chemical Kinetics Determination via Stirred Reactor Test

DESCRIPTION

The chemical kinetics via stirred reactor test is the measure of a decontaminant capability to reduce agent in a well-mixed system in the absence of material effects. The test can be executed to determine either reaction kinetics or endpoint. This section contains the original procedure documented in TOP 8-2-061 (Initial Release) dated November 19, 2002. This test was not updated as part of the FY06-07 test program. The method is included for completeness and as applicable, test reporting recommendations were added.

CONTENTS

4A - Decontaminant Neutralization via Stirred Reactor Test

Test Procedure 4-A: Chemical Kinetics Determination via Stirred Reactor Test

SUMMARY OF PROCEDURE

The chemical kinetics via stirred reactor test is the measure of a decontaminant capability to reduce contaminant in a well-mixed system in the absence of material effects. The test can be executed to determine either reaction kinetics or endpoint. This section contains the original procedure documented in TOP 8-2-061 (Initial Release) dated November 19, 2002. This test was not updated as part of the FY06-07 test program. The method is included for completeness and as applicable, test reporting recommendations were added.

TERMINOLOGY

Terminology specific to this test method include:

- **Contaminant:** A chemical species with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **Analytical Sample:** Liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **Quench Compound:** Substance used to neutralize the decontaminant active component to stop further reaction.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** the specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
  - <u>Chemical Agent</u>: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents that can be tested may include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
  - <u>Chemical Agent Simulant</u>: Chemical agent simulants are compounds of lower toxicity that contain at least one similarity to the live chemical agent. Since these materials are of lower toxicity, the compounds do not contain all of the same physical and chemical properties of the live agent. Simulants should be selected based on the main property being tested for most accurate comparison. Appendix B contains a general listing of commonly used chemical agent simulants.

- Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.

- **Decontaminants:** the specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants used are liquid-phase. A general listing of chemical decontaminants is provided in Appendix B.
- **Quench Compound:** sodium sulfite, sodium carbonate.

MATERIALS AND EQUIPMENT

- **Standard Laboratory Record Keeping Items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **General Laboratory Items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper toweling, beakers, vials, spatulas, parafilm, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatography equipment. The vial cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.
- **Reaction vessel**: jacketed laboratory glassware of sufficient volume to hold up to 50 mL of decontaminant and 1 mL of contaminant, stirring device.
- Pipette
- Analytical equipment such as GC-MS or LC-MS.
- **Optional Items:** Items that may be used include analytical balance, stir plate, stir bars, pH meter.

ADDITIONAL SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

a. General

(1) This test determines the time it takes for a decontaminant to neutralize chemical agent in a reaction vessel.

(2) Quantities of decontaminant and chemical agent may be varied as directed by the test sponsor based on recommendations from the decontaminant manufacturer.

b. Freshly-prepared decontaminant (50 mL) will be placed into a stirred, jacketed reaction vessel maintained at 25 °C (77 °F). The stirrer will be started and the contents allowed to thermally equilibrate.

c. The reaction will be initiated by adding 1.00 mL of agent and the time will be noted (t=0).

d. The stirring rate will be adjusted as necessary to ensure complete mixing and homogenous humidity.
e. At measured intervals (standard will be every 2 min for first 10 min, and every 5 min thereafter until a total of 1 hr elapsed time after agent addition) starting at t=2 min, a 50 µL sample will be collected for GC-AED or GC-MS analysis. The sample will be added to vials containing the quench solution and 2.00 mL of chloroform. This mixture will be vigorously agitated using a vortex mixer, and then the phases will be allowed to separate.

(1) For soman (GD) and distilled mustard (HD), the quench solution is 0.2 M sodium sulfite in water.

(2) For persistent nerve agent (VX), the quench solution is 0.2 M sodium sulfite and 0.2 M sodium carbonate. The sodium sulfite is present to destroy any residual oxidant while the sodium carbonate is present to make certain that the amine group on the VX is entirely in the free base form needed for complete extraction into the chloroform.

f. Using a micropipette, 1.0 mL of the chloroform layer will be transferred to an auto sampler vial.
g. The sample will be analyzed with GC-AED or GC-MS.

TEST REPORTING

h. The following data will be reported:

(1) GC results, including amount of agent and reaction products

(2) Amount of agent remaining at each sample time, and the time required for agent to become undetectable (if it becomes undetectable).

(3) Observations during reaction. Observations should include visual inspection for HD droplets in the decontaminant.

(4) pH.

(5) Mass of agent applied and agent purity.

(6) TICN, SICN, and control results.

(7) Test conditions to include reactor solution temperature, room temperature ,and room relative humidity.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

None.

REVISION HISTORY

March 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional

guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method and are shown in underlined, italicized text.

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Section 5: Material Compatibility Testing

DESCRIPTION

The material compatibility tests are used to determine the impact the decontaminant has on the material integrity or ability to perform intended function. These tests are typically based on standardized methods. These tests are typically conducted on materials that have not been contaminated since the amount of decontaminant is significantly greater than the amount of contaminant. These tests could be performed on materials that have been contaminated and decontaminated under appropriate engineering controls. This section does not provide step-by-step procedures for the contamination of materials. The 2002 TOP 8-2-061 and FY07 Source Document do not capture all of the material integrity or compatibility tests that may be of interest to the test sponsor for a given application. Standardized methods should be used when possible. Guidance for the use of standardized test methods outside of the ones specifically included was provided in the FY07 Source Document.

CONTENTS

5A - Metal Corrosion Test Method*

5B - Sorption (Elastomer)/Hardness (Elastomer) Test Method*

5C - Sorption (Thermoplastic)/Haze and Transmittance (Thermoplastic) Test Method*

5D - Hardness (Coating) Test Method*

5E - Guidance for the Use of Standardized Test Methods for Decontaminant Evaluations

NOTES

*Method not updated as part of FY06-FY07 effort.

Test Procedure 5-A: Metal Corrosion Test Method

SUMMARY OF PROCEDURE

Metal corrosion is determined using ASTM test method G31-72 (reapproved 2004) "Standard Practice for Laboratory Immersion Corrosion Testing of Metals." This method describes the accepted procedures for preparing specimens, identifying test apparatus and test conditions, cleaning methods, evaluating results, calculating and reporting corrosion rates. This method identifies these procedures as having influence on laboratory immersion corrosion tests, especially for the determination of mass loss. The mass loss can be calculated and is reported in units of milligrams (mg). The corrosion rate can be calculated and is reported in units of mils-per-year (mpy).

TERMINOLOGY

Terminology specific to this test method include:

- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **Coupon:** Test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. Sometimes the word panel is used interchangeably with coupon.
- **Coupon Handling:** Treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- American Society for Testing and Materials (ASTM), Standard Practice for Laboratory Immersion Corrosion Testing of Metals, ASTM Document Number G31-72 (Reapproved May 2004).
- American Society for Testing and Materials (ASTM), Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, ASTM Document Number G1-03.
- American Society for Testing and Materials (ASTM), Standard Guide for Applying Statistics to Analysis of Corrosion Data, ASTM Document Number G16-95 (Reapproved 2004).
- American Society for Testing and Materials (ASTM), Standard Guide for Examination and Evaluation of Pitting Corrosion, ASTM Document Number G46-94 (Reapproved May 2005).

REAGENTS, MATERIALS AND EQUIPMENT

This listing of reagents, materials and equipment is a general listing based on the tools needed for conducting the ASTM method in a chemical laboratory. This list is not considered complete and the ASTM should be consulted for any additional reagents, materials or equipment needed.

REAGENTS, MATERIALS AND EQUIPMENT

- **Coupons:** Test sample representative material surface.
- **Decontaminants:** the specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants typically can be liquid-, solid- and vapor-phase and may contain a reactive functionality for also neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Timing device**
- **Test containers**: Apparatus / method for containing solution and suspending coupon.
- **Specimen cleaning supplies**: necessary brushes, tools and cleaning solution for post test cleaning of specimens.
- **Analytical balance**
- **Caliper**
- **Pit gage**
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper toweling, beakers, vials, spatulas, parafilm, etc.
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, pH meter, digital camera, data logger to record temperature.
- **Personal protective equipment:** Material Safety Data Sheets should be consulted to determine specific personal protective equipment requirements for materials used during testing. In addition, test facility may require additional equipment. At a minimum in any laboratory an approved lab coat and eye protection, and appropriate gloves are to be worn.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE GUIDANCE

The ASTM method is a copyrighted document by ASTM International that cannot be reproduced without licensed permission. The specific procedure for this test is documented in ASTM G31-72. This section captures key guidance from the procedure related to decontaminant testing.

Materials: Standard does note that for some metals, such as titanium and zirconium, the corrosion produces a hard and tightly bonded oxide that cannot be easily removed by standard chemical or mechanical methods. For these cases, the change in mass is reported as a mass gain rather than a mass loss.

Immersion: Samples can be tested as full immersion, partial immersion, or vapor exposed. The selection is dependent on the test goals; however, the sample must be supported vertically. Samples should not rest horizontally in the test apparatus.

Calibration: method uses measurement tools such as balance, calipers and pit gage. These tools should be properly maintained, calibrated and checked on an appropriate schedule, typically annually. The use of certified weights to confirm balance operation prior to sample measurements is encouraged.

Test Duration Guidance:

- General guidance: the test duration should not be so long that the specimen size is drastically reduced.
- Immersion Time and Corrosion resistant metal and alloy evaluations: The 2002 TOP 8-2-061 specifies a 24-hour immersion time. The ASTM standard states that short-time duration tests can give misleading results for metals such as stainless steel. Some metals and alloys form passive films requiring longer immersion times to accurately assess corrosion rates. The ASTM standard provides guidance for selecting the time duration. The standard states the most common testing periods are 48 to 168 hours (2 to 7 days). If shorter times are used, the results may be limited to express corrosion only for the length of time studied; data extrapolation might be limited.
- Planned interval test: the ASTM standard provides guidance for test strategies that remove corrosion products between exposure periods. Guidance is provided in the ASTM standard for the proper execution of this test variation.

Related Test Standards: These following standards provide additional procedures that may be employed during corrosion testing depending on the specific test objectives.

- ASTM method G1-03 "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens" provides procedures for specimen preparation, removing corrosion products and evaluating corrosion damage. The methods are focused on mass loss and pitting measurements.
- ASTM method G16-95 "Standard Guide for Applying Statistics to Analysis of Corrosion Data" provides some generally accepted methods for statistical analysis of corrosion data. The standard does not provide detailed calculations.
- ASTM method G46-94 "Standard Guide for Examination and Evaluation of Pitting Corrosion" provides information regarding the identification, naming, examination and evaluation of pitting from corrosion testing.

TEST REPORTING

The following information is to be documented for each test and in the final technical report:

- All of the required reporting criteria in ASTM G31-72, Section 12

- A description of the specific apparatus used from the options provided in ASTM G31-72, Section 5.
- The decontaminant tested including date and time of preparation.
- Summary of any changes / modification to the ASTM method during execution. The documentation of these deviations is important to capture context that may explain differences in lab-to-lab data.
- If related test standards are use, the method should be cited and the method reporting requirements documented.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Laboratories are encouraged to establish data acceptance criteria and corrective action. This ASTM method does not specify precision or bias for the execution of this test. ASTM method G31-72 does state that under the same test conditions, replicate sample corrosion rates are typically within ±10 %.

CALCULATIONS

The calculations for this test method are documented in ASTM method G31-72, Section 11.

REVISION HISTORY

March 2008: This test utilizes an ASTM standard test method. This method was used as part of a different FY07 decontamination program. The methods were added to the Source Document to include FY07 program review learnings and updated test documentation requirements to ensure pertinent information is recorded during testing. The procedure was not reproduced as the ASTM is a copyrighted document.

Test Procedure 5-B: Sorption (Elastomer)/Hardness (Elastomer) Test Method

SUMMARY OF PROCEDURE

Elastomer hardness can be determined using ASTM test method D 2240-05 "Standard Test Method for Rubber Property – Durometer Hardness." This method measures the force required to create an indentation for a material. Appropriate materials for this test include thermoplastic elastomers, vulcanized (thermoset) rubber, elastomeric materials, cellular materials, gel-like materials, and some plastics. This test provides a hardness measurement.

ASTM test method D 471-06 "Standard Test Method for Rubber Property – Effect of Liquids" measures the comparative ability of rubber materials to withstand the effects of liquid contact. Some of the physical characteristics covered by this method include change in mass, volume, dimension, and tensile strength either due to immersion or surface contact. The method is divided into seven sub-tests.

TERMINOLOGY

Terminology specific to this test method include:

- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **Coupon:** Test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. Sometimes the word panel is used interchangeably with coupon.
- **Coupon Handling:** Treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- American Society for Testing and Materials (ASTM), Standard Test Method for Rubber Property-Effect of Liquids, ASTM Document Number D471-06, 1 October 2006.
- American Society for Testing and Materials (ASTM), Standard Test Method for Rubber Property-Durometer Hardness, ASTM Document Number D2240-05, 15 August, 2005.

REAGENTS, MATERIALS AND EQUIPMENT

This listing of reagents, materials and equipment is a general listing based on the tools needed for conducting the ASTM method in a chemical laboratory. This list is not considered complete and the ASTM should be consulted for any additional reagents, materials or equipment needed. This particular ASTM requires that "all materials, instruments, or equipment used for the determination of mass, force, or dimension shall have traceability to the National Institute for Standards and Technology, or other internationally recognized organizations parallel in nature."

REAGENTS, MATERIALS AND EQUIPMENT

- **Coupons:** Test sample representative material surface.
- **Decontaminants:** the specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants typically can be liquid-, solid- and vapor-phase and may contain a reactive functionality for also neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Durometer**
- **Analytical balance**
- **Caliper**
- **Temperature sensor**
- **Humidity Sensor**
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper toweling, beakers, vials, spatulas, parafilm, etc.
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, pH meter, digital camera, data logger to record temperature.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE GUIDANCE

The ASTM method is a copyrighted document by ASTM International that cannot be reproduced without licensed permission. The specific procedure for this test is documented in ASTM D 2240-05. This method emphasizes the needs for measuring the environmental conditions (temperature and relative humidity) during testing and the confirmation that test equipment is calibrated.

Recommended practice: conduct a control test using a material of known hardness to confirm operator and durometer performance prior to the start of testing.

TEST REPORTING

The following information is to be documented for each test and in the final technical report:

- All of the required reporting criteria in ASTM D 2240-05, Section 10.
  - Note, the reporting instructions emphasize documentation of the durometer calibration status.
- The sections performed from ASTM D 471-06.
- The appropriate reporting criteria from ASTM D 471-06, Section 18.
- The decontaminant tested including date and time of preparation.
- Summary of any changes / modification to the ASTM method during execution. The documentation of these deviations is important to capture context that may explain differences in lab-to-lab data.
- If related test standards are used, the method should be cited and the method reporting requirements documented.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Laboratories are encouraged to establish data acceptance criteria and corrective action. ASTM method D 2240-05 does provide some guidance for precision, repeatability and reproducibility. ASTM method D 471-06 does provide some guidance for precision, repeatability and reproducibility in Section 19. These criteria should be consulted and applied as appropriate.

CALCULATIONS

No specific calculations are required ASTM method D 2240-05.

The calculations for ASTM method D 471-06 are provided in Section 17.

REVISION HISTORY

March 2008: This test utilizes an ASTM standard test method. The procedure was not reproduced as the ASTM is a copyrighted document. This method was not reviewed as part of a different FY07 program. The Source Document method includes learnings from the review applicable to decontaminant evaluations. The methods were added in the Source Document format. The methods were updated to include additional requirements for the test documentation to ensure pertinent information is recorded during testing.

Test Procedure 5-C: Sorption (Thermoplastic)/Haze and Transmittance (Thermoplastic) Test Method

SUMMARY OF PROCEDURE

ASTM test method D543-06 "Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents" covers the reporting of changes in weight, dimensions, appearance and strength properties for plastic materials contacted with chemical reagents. ASTM test method D1003-00 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics" is the evaluation of luminous transmittance and haze. The method contains two procedures for the use of either a hazemeter or spectrophotometer. The haze and transmittance are reported in percent. In decontaminant evaluations, it may be desired to conduct the chemical reagent test, and then evaluate for haze and transmittance. Although these methods are written for plastic materials, these methods have been applied in the open literature and patents for the evaluation of laminate coated glass, certain ceramics and glass. These methods may be applicable to other viewport materials.

TERMINOLOGY

Terminology specific to this test method include:

- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **Coupon:** Test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. Sometimes the word panel is used interchangeably with coupon.
- **Coupon Handling:** Treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- American Society for Testing and Materials (ASTM), Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents, ASTM Document Number D543-06, 1 April 2006 (June 2006 – published)1 August 1995.
- American Society for Testing and Materials (ASTM), Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics, ASTM Document Number D1003-00, 10 June 2000, (July 2000-published) 1 August 2000.

REAGENTS, MATERIALS AND EQUIPMENT

This listing of reagents, materials and equipment is a general listing based on the tools needed for conducting the ASTM method in a chemical laboratory. This list is not considered complete and the ASTM should be consulted for any additional reagents, materials or equipment needed.

REAGENTS, MATERIALS AND EQUIPMENT

- **Coupons:** Test sample representative material surface.
- **Decontaminants:** the specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants typically can be liquid-, solid- and vapor-phase and may contain a reactive functionality for also neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Analytical balance**
- **Caliper**
- **Hazemeter or spectrophotometer**
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper toweling, beakers, vials, spatulas, parafilm, etc.
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, pH meter, digital camera, data logger to record temperature.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE GUIDANCE

The ASTM method is a copyrighted document by ASTM International that cannot be reproduced without licensed permission. The specific procedure for this test is documented in ASTM D 1003-00 and ASTM D 543-06.

TEST REPORTING

The following information is to be documented for each test and in the final technical report for ASTM test method D1003-00:

- Indication as to whether hazemeter or spectrophotometer were used
- All of the required reporting criteria which are Section 7.4 for hazemeter and/or Section 8.4 for spectrophotometer.
- The decontaminant tested including date and time of preparation.
- Summary of any changes / modification to the ASTM method during execution. The documentation of these deviations is important to capture context that may explain differences in lab-to-lab data.

The following information is to be documented for each test and in the final technical report for ASTM test method D 543-06:

- The specific test sections performed.
- All of the required reporting criteria in Section 20.
- The decontaminant tested including date and time of preparation.
- Summary of any changes / modification to the ASTM method during execution. The documentation of these deviations is important to capture context that may explain differences in test-to-test and lab-to-lab data.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Laboratories are encouraged to establish data acceptance criteria and corrective action. ASTM test method D 1003-00 provides some guidance for precision, repeatability and reproducibility in Section 7 for the hazemeter measurement and Section 8 for the spectrophotometer measurement. ASTM D 543-06 does not provide precision guidance as the performance of plastics against the standard reagent list can widely vary.

CALCULATIONS

ASTM test method D 1003-00 provides hazemeter calculations for determining total and diffuse transmittance in Section 7.3.

REVISION HISTORY

March 2008: This test utilizes an ASTM standard test method. The procedure was not reproduced as the ASTM is a copyrighted document. This method was reviewed as part of a different FY07 program. The Source Document method includes learnings from the review applicable to decontaminant evaluations. The methods were added in the Source Document format. The methods were updated to include additional requirements for the test documentation to ensure pertinent information is recorded during testing.

Test Procedure 5-D: Hardness (Coating) Test Method

SUMMARY OF PROCEDURE

ASTM test method D 3363-05 "Standard Test Method for Film Hardness by Pencil Test" is a simple procedure for determining the film hardness of an organic coating. The method uses a set of calibrated drawing pencils that range in lead hardness.

TERMINOLOGY

Terminology specific to this test method include:

- **Decontaminant:** For these procedures, a substance with capability to remove and/or neutralize chemical agents on / in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), gas-phase (fumigants). A summary list of decontaminants is provided in Appendix B.
- **Coupon:** Test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. Sometimes the word panel is used interchangeably with coupon.
- **Coupon handling:** Treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- American Society for Testing and Materials (ASTM), Standard Test Method for Film Hardness by Pencil Test, ASTM Document Number D3363-05, 1 January 2005.

REAGENTS, MATERIALS AND EQUIPMENT

This listing of reagents, materials and equipment is a general listing based on the tools needed for conducting the ASTM method in a chemical laboratory. This list is not considered complete and the ASTM should be consulted for any additional reagents, materials or equipment needed.

REAGENTS, MATERIALS AND EQUIPMENT

- **Coupons:** Test sample representative material surface.
- **Decontaminants:** the specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants typically can be liquid-, solid- and vapor-phase and may contain a reactive functionality for also neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Calibrated pencil set**
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE GUIDANCE

The ASTM method is a copyrighted document by ASTM International that cannot be reproduced without licensed permission. The specific procedure for this test is documented in ASTM D 3363-05. For decontaminant applications, the recommended approach is to compare the change in film hardness by determining the film hardness for the untested panel. If the decontamination process utilizes brushing or other surface mechanical / physical operations, there may be interest in separating the effect of the decontaminant from the applicator process. These types of process isolation steps may be useful in certain evaluations.

TEST REPORTING

The following information is to be documented for each test and in the final technical report:

- All of the required reporting criteria in ASTM D 3363-05, Section 8.
- The panel film preparation details including:
    - Film application such as MIL procedures followed and any deviations in standard procedure.
    - Coating age
- The panel history prior to testing including
    - Cleaning or other surface preparation prior to testing
    - Contamination process details is contaminants used
    - Decontamination process details
- The decontaminant tested including date and time of preparation.
- Summary of any changes / modification to the ASTM method during execution. The documentation of these deviations is important to capture context that may explain differences in lab-to-lab data.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Laboratories are encouraged to establish data acceptance criteria and corrective action. This ASTM test method does indicate that this test can be variable between laboratories, panels and operators. The test is best suited within a single laboratory when many of these variables can be strictly controlled. The standard provides precision, repeatability and reproducibility guidance. A laboratory with multiple operators should know lab precision and repeatability.

CALCULATIONS

There are no specific calculations for this method.

REVISION HISTORY

March 2008: This test utilizes an ASTM standard test method. The procedure was not reproduced as the ASTM is a copyrighted document. This method was not reviewed during the FY07 program to identify necessary additions for the application to decontaminant evaluations. The methods were added in the Source Document format. The methods were updated to include additional requirements for the test documentation to ensure pertinent information is recorded during testing.

Test Procedure 5-E: Guidance for the Use of Standardized Test Methods for Decontaminant Evaluations

In addition, The ASTM methods presented in this chapter were those identified in TOP 8-2-061 initial release. This list is not intended to fully encompass the tests that may be required based on an intended acquisition program, final use platform (i.e., vehicles, planes, buildings, equipment, etc.), or program material list. There are many standardized methods that could be employed in decontaminant evaluations based on the material of interest.

Quite often in decontaminant literature, thorough documentation of how the method was executed is not provided. This lack of information can create confusion when data is compared over the course of development or between laboratories. Recommendations to facilitate the use of decontaminant data to assess material compatibility include:

- **Materials**: Provide detailed source and sample preparation details. Whenever possible, obtain vendor specification sheets for stock material used to prepare test samples.
- **Contaminants**: the documentation should include the contaminants tested, source, lot and purity.
- **Decontaminants**: the documentation should include decontaminants tested, source, lot (if available), date or preparation or expiration date. For R&D evaluations, the decontaminant or applicator model / version number should be noted, as changes in formulation or applicator may require revisiting of selected material compatibility tests later in the development program.
- **Sample History**: The report should include the sample treatment from start up to material compatibility testing for completeness.
- **Material Control Tests**: A material control test is recommended for most material compatibility tests. This is the evaluation of the test material that has not been treated with contaminant or decontaminant. This test provides a measure of the material integrity for the starting material. In many cases, this value provides a reference for the determination of the degree of material degradation incurred during the treatment process. This test can provide data comparison context if sample preparation or test execution affect test result.
- **Comparison to Specification Sheets**: Specification sheets can be obtained for some materials, especially metals, from the vendor. These specification sheets may contain the minimum requirements per some of the ASTM tests. For example, the tensile strength per ASTM A 240 can be obtained for most metals. If this test is performed in the laboratory and the material control tests do not meet this specification, this is typically an indication that the sample preparation or test was not executed in accordance with the method. If method deviations are clearly documented, it may be suitable to perform the test using the material control as the comparative sample to determine degree of material degradation.
- **Process Isolation Tests**: for some applications it may be of interest to evaluate the performance of the decontaminant, applicator and process (i.e., brushing or scrubbing) independently to determine which process step contributes most to observed material incompatibilities. Process isolation tests are recommended for this case. The process variations should be clearly documented and the material compatibility test method should not deviate between process isolations evaluations so that the process, not the test method changes, is evaluated.

- **Documented deviations from test method:** all deviations from the written standard should be documented. It is anticipated that for certain applications, minor modifications may need to be made to achieve test objectives. Documenting that a test was done based on a test method with clearly documented test modifications provides the user of the data the ability to determine appropriate data use, context and comparability.

Section 6: Panel Contact Test to Determine Contact Hazard

DESCRIPTION

The contact test series contains the procedures for the measurement of agent present after the decontamination process that could pose a hazard through transfer to skin. These tests utilize a contact sampler as a surrogate for human skin, coupons of operationally relevant materials, solvent extraction, and chromatographic analytical methods. The rigorous laboratory-scale test method uses a standard a two in. diameter circular coupon. The methods can be applied to larger coupons and test articles. These tests evaluate liquid agent challenges against decontaminants in liquid-, solid- or vapor-form. The experimental test data can be converted to a contact hazard value in units of mg/m^2.

CONTENTS

6A - Laboratory-Scale Decontaminant Performance Evaluation for Contact Test Method

6B - Contact Sampler Extraction- and Sampling-Efficiency Test Method

6C - Rinsate Analysis for Agent Test Method[1]

6D - Baseline Contact Test Method

6E - Panel (Coupon) Extraction Method to Determine Remaining Agent

6F - Panel (Coupon) Extraction Efficiency Test Method

6G - Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy or Reduction in Starting Challenge

6H - Chromatographic Analysis Guidance

NOTES

[1] Denotes method being developed as part of FY08 effort for program CA07DEC420.

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Test Procedure 6-A: Laboratory-Scale Decontaminant Performance Evaluation for Contact Test Method

SUMMARY OF PROCEDURE

The contact test is the measure of the contaminant present after the decontamination process that could pose a hazard through transfer to skin or other surfaces. A contact sampler is used in this test as a surrogate for human skin. The contact sampler is used to collect the agent from the coupon surface. A contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). The contact sampler is extracted, and the contamination collected during a touch is quantified. The contact test simulates the interaction of skin with the surface of interest. This measure of contamination is not the full residual agent; but rather, a measure of the contamination that could be bioavailable by touch or available for contact transfer. **The laboratory-scale Decontamination Performance Evaluation for contact-hazard measurement is a rigorous method for the execution of decontamination testing using a standard two in. disk coupon.** This method can be used to evaluate decontaminant performance against liquid-phase contaminants such as chemical-warfare agents, chemical-warfare agent simulants, toxic-industrial-chemicals, and toxic-industrial-materials. The terms contaminant and agent are used interchangeably. This test is for the dry-skin case.

This procedure provides the following information:

- **The mass of contaminant in nanograms recovered from the contact sampler after the decontamination process**.
- **The mass of agent in nanograms recovered from the coupon after the decontamination process and contact test.**
- This test may also provide the mass of agent by-products in nanograms recovered from the contact sampler if appropriate analytical methods are used.

The following prerequisite tests are required for this test procedure:

- Procedure 6-B, "Contact Sampler Extraction- and Sampling-Efficiency Test Method" is the method for determining the extraction efficiency of residual agent in or on the contact sampler using the solvent selected for testing.
- Procedure 6-F, "Panel (Coupon) Extraction Efficiency Test Method" is the method for determining the efficiency the selected solvent has for recovering agent from the coupon.
- Procedure 6-H, "Chromatographic Analysis Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

This procedure alone does not provide the complete assessment of the decontaminant's performance for reducing the agent contamination or reporting the hazard. The complete assessment of a decontaminant performance should also address:

- The amount of agent physically removed from the coupon during the decontamination process using either liquid decontaminants or post-decontamination rinsing step.
    - Procedure 6-C, "Rinsate Analysis for Agent Test Method" is the measurement of the amount of agent physically removed from the coupon during the decontamination process.
- The determination of percent neutralization and reduction in starting challenge is best addressed through the direct measurement of the amount of remaining agent.

- Procedure 6-E, "Panel (Coupon) Extraction Method to Determine Remaining Agent" is the process for extracting, measuring and reporting the residual agent in or on the coupon.
- The amount of agent lost during the decontamination process to weathering / evaporation.
  - Procedure 6-D, "Baseline Contact Test Method," is the method for conducting the decontamination process without the use of decontaminant.
- Reporting the contact hazard value in mg/m^2.
  - Procedure 6-G, "Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy, or Reduction in Starting Challenge" is the process for converting the mass of agent recovered from the contact sampler to a reported hazard value.
- Reporting percent neutralization, percent efficacy, or reduction in starting challenge in g/m^2.
  - Procedure 6-G, "Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy, or Reduction in Starting Challenge" is the process for converting the mass of agent recovered from the contact sampler to a reported hazard value.

Limitations and other test variations:

- This complete process provides the contact-test result for the first 60 min after decontamination. The hazard for 24 hours post decontamination cannot always be assumed the same as the 60 minute value.
  - Sorptive / porous materials: Re-emergence of entrained agent from sorptive materials may pose future hazard. The residual agent extraction test is recommended to identify the potential future hazard. Sorptive materials will typically have significant residual agent post-decontamination requiring the proper documentation that a potential hazard may exist beyond the timepoint studied. If residual agent is present, then the contact-hazard at times beyond those tested must be reported as uncertain. As a result, the current guidance for many of these materials is replacement if contaminated.
  - Nonsorptive materials: Nonsoprtive materials typically yield low to no-detectable residual agent, which may allow for time extrapolation of the 60 minute value out to longer time periods. A reported value that is an estimate or extrapolation outside the collected dataset must be clearly marked as such.
- Contaminant Simulant: chemical compounds for chemical agents are often used during early screening, or at non-chemical agent surety facilities. A chemical agent simulant is a chemical compound of lower toxicity than the chemical agent with at least one property similar to the chemical agent, such as certain bonding, functional group, physical property, etc. Simulants should be selected based on the main property being tested for most accurate comparison. Since simulants do not contain all of the same physical and chemical properties of the live agent; simulant data alone is not sufficient to determine decontaminant performance. It is recommended that the simulant performance be confirmed with agent data.
- Skin Simulant: The ability to test every decontaminant–contaminant–material combination on real skin is not realistic. A skin simulant is used to estimate the contaminant transfer that may occur if the surface of interest was contacted with real skin. The selection of the contact sampler is not trivial, as this ability to

emulate skin requires careful consideration. The recommended material per reported toxicology information is latex dental dam, preferably unflavored, uncolored, and heavy gauge (0.01 in. thick). The use of materials with properties significantly different than skin may result in the collection of more or less agent. Comparison of data using different contact samplers should factor in the material uptake characteristics in the interpretation of the results.

- This test method is specifically for the dry-skin sampling case. Toxicological data has shown that the uptake on wet skin tends to be greater than dry skin. When evaluating data for specific situations, the risk for wet skin contact should be considered.
- Certain variations fall outside the scope of the Laboratory-Scale Performance Evaluation test methods. This test method is only directly applicable to panels, items or other test surfaces that can be sampled with the contact sampler and mass, and extracted in solvent. Complex coupons or articles requiring wiping or alternate swabbing procedures are outside the scope of this method.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA). In this case the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample** - liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **bioavailable –** in toxicology, the degree to which a substance becomes available to the target tissue after administration of a defined exposure. In regard to the contact test, the contaminant mass transferred to the contact sampler that could be biologically available under appropriate conditions.
- **breadboard, brassboard, prototype** – technology in differing degrees of configuration still under development that is not in final form. This can apply to test fixtures, formulations and/or the decontamination system / applicator.
- **chemical agent** - is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contact hazard -** the amount of contaminant remaining on the surface that, based on toxicological human estimates, could pose a threat to unprotected personnel touching the contaminated surface.
- **contact mass -** a uniform mass used to apply pressure during the contact test. The masses are typically prepared from stainless steel. The masses should evenly exert

0.7-1.0 psi (0.05-0.07 kg/cm^2) pressure on the coupon surface. For the 2 in. diameter disk, this is equivalent to a 2 in. diameter cylindrical mass weighing 1 kg.

- **contact sampler -** material used in this contact test as a surrogate for human skin. The sampler sorbs the available surface contamination which is then extracted to determine the mass of agent potentially bioavailable or available for contact transfer.
- **contact sampler transfer efficiency -** the measurement of the contact sampler's ability to collect the contaminant from the test material (e.g., coupon). More specifically, the contact sampler's ability to sorb the analyte under the ideal case by using a nonsorptive material. Transfer efficiency may be different for material-agent combinations.
- **contact transfer -** the capability for a contaminant present on a specific surface to be moved to another through touching the contaminated surface.
- **contaminant -** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemicals, and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant -** for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process -** The process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically for these procedures, the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing, and drying.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes

cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.

- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency** - the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **foam** - spongelike material used in the contact test to ensure contact mass pressure is evenly applied to the test surface.
- **hazard** - A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*
- **moderate condition** - test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization** - the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **operational decontamination** – decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material and/or working areas, in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **percent efficacy (and calculation)** - the measurement of the amount of contaminant removed from the material of interest as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **percent neutralization (and calculation)** - the measurement of the amount of contaminant reacted/neutralized as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **reduction in starting challenge (and calculation)** – the measurement of the mass of contaminant that has been removed from the material of interest. This calculation is

most often employed for the evaluation of physical removal, sorbent, or pre-clean techniques. The value can be reported as calculated, approximated, or inferred.

- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **remaining agent** - the amount of contaminant present in / on the material of interest after the decontamination process has been conducted. This value is different from the residual agent in that no mass has been removed from the coupon by contact or vapor testing. This value cannot be used to calculate a contact- or vapor-hazard.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate** - the collected rinse from the decontamination process. Sample may include residual decontaminant, agent, and agent byproducts in water.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface it is better described as a thin film.
- **skin simulant** – material used in the contact test to estimate the contaminant transfer that may occur if the surface of interest was contacted (e.g., touched) by real skin. See test limitations regarding use for contact testing.
- **sorptive or porous materials** - a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition** - for a specific agent – material- decon set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **touch** - a contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration and skin condition (wet versus dry). For the coupon test, the contact area is nominally the coupon area. The pressure is 0.7 to 1.0 psi (0.05-0.07 kg/cm^2) pressure which is equivalent to a 1 kg contact mass that is cylindrical with a 2 in. diameter. The contact time is typically 15 min.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-5, Nuclear, Biological, and Chemical (NBC) Decontamination, 17 November 1993.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.5, Multiservice Tactics, Techniques, and Procedures for Chemical, Biological,

Radiological, and Nuclear Decontamination Nuclear, Biological, and Chemical (NBC) Decontamination, 4 April 2006

- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.9, Potential Military Chemical/Biological Agents and Compounds, 10 January 2005.
- Headquarters, Department of the Army (DA), Washington, DC, Army Manual (AR) 70-38, Research, Development, Test and Evaluation of Materiel for Extreme Climatic Conditions, 15 September 1979.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
  - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
  - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
  - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Decontaminants:** The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid- or vapor-phase and may contain a reactive functionality for neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Extraction solvents:** The test requires the extraction of sorbed agent from test materials such as the contact sampler and/or coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride, and solvent blends.
- **Water:** Decon processes typically involve a post-rinse step and some decontaminants are made using water. Laboratory testing will use distilled or deionized water unless otherwise instructed by the test sponsor.

EQUIPMENT

The equipment required for this method includes tools for delivering contaminant, decontaminant, and rinse water; maintaining environmental control and preparing analytical samples. Several equipment options exist, ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision, and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a two inch diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (µL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 µL delivered as two 1 µL drops for a 1 g/m^2 starting challenge.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. These are also best suited for pipetting volatile liquids. The smallest delivery volume, based on survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured. Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. The smallest delivery volume based on survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
    - Computerized Dispensing System: Automated tool with ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.
- **Decontaminant Delivery Tool:** the tool used to deliver a specific volume of decontaminant to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The core coupon test

specifies using a decontaminant volume of 0.100 to 1.00 mL. The specific decontaminant under evaluation may use other delivery volumes.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of decontaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
- Spray Bottle: Some applications will mimic a spray application using a spray bottle. The tool should be evaluated to determine the number of pumping actions required to achieve target decontaminant application. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- Developmental Breadboard, Brassboard or Prototype Technology: These are technologies under development that are not the in final configuration. The decontaminant generation and delivery may not be known. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- Vendor Provided Technology: This is equipment provided from vendor that may be breadboard, brassboard, prototype, or commercial in configuration. The technology is operated per vendor guidance. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Water Rinse Delivery Tool:** Tool for the delivery of specific volumes of water to the coupon surface to remove decontaminant from the surface. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. It is recommended that the tool used has ability to control flow rate in order to reduce operator-to-operator variations. The typical delivery volume for a 2 in. diameter circular contamination area range is 60 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. An example is the Dispensette and Brinkman brands. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.

- Pump: Other precision liquid dispensing systems. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
    - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.

- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
    - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.

- **Temperature Controlled Surface for Contact Test:** The lab-scale testing uses a temperature controlled surface to mimic body temperature regulated at 30 °C (86 °F).
    - Slidewarmer: temperature controllable surface typically used in histological testing. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information must be tested to determine their accuracy and precision.

- **Environmental Chamber:** Temperature and relative humidity controlled chamber for the preconditioning and aging of coupons. Fixtures should be able to maintain test specific environmental conditions (e.g., temperature and relative

humidity) even when adding or removing samples. The system must have temperature and relative humidity data logger capability, be able to store and download temperature and humidity data and traces to a computer for further analysis. The system must be able to maintain temperature and relative humidity. The system operation and range should be known.

- **Contaminated Area Measurement:** Fixed-site photographic setup to visually capture the agent contamination surface area coverage after dosing, aging and any other critical steps in the decontamination process. A photograph resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation.
    - <u>Digital Camera on Fixed Stand</u>
    - <u>Imaging Station</u>
- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Method 6-H. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space, protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Contact mass(es):** Laboratory scale contact test utilizes a mass to deliver 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure during the contact touch. For the 2 in. disk, the mass is a stainless steel, 2 in. in diameter cylinder weighing 1 kg placed onto the sample surface for the duration of the contact time.
- **Contact sampler(s):** Adsorptive material used to collect available contamination from surface of interest. The use of latex dental dam, preferably unflavored, uncolored, and heavy gauge is suggested. Testing will typically use 0.01 in. thick material.
- **Coupon(s):** Test sample representative of the material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials, caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains an excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the contact sampler and/or coupon. A glass container such as a vial or jar of sufficient size to hold both the contact sampler and/or coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommended for chemical agent testing.

- **Foam**
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** typically used during the aging step to cover the coupon surface to minimize evaporative loss. Can also be used as sample holder.
- **Rinsate collection container:** If rinse water analysis is required, the rinse should be collected in a glass container of sufficient volume for the rinse water and extraction solvent, preferably a wide mouth jar. It is recommended to limit the use of funnels or other tools that may uptake agent during collection. Use of plastic containers is not recommended for chemical agent testing. The container cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers, or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks, and writing utensils.
- **Transfer pipettes**
- **Timing device(s):** Test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, and pH meter.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement, and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.

This test has Options A, B and C that are step variations based on potential variables that could be explored. The core test evaluation is designated by Option A. This option is based on a liquid decontaminant tested at moderate environmental conditions using equipment with known accuracy. This option should be used unless otherwise instructed by a test sponsor. Option B is similar to Option A but allows for different parameters, such as temperature. Option C is designed for the evaluation of new technologies or the use of conditions outside of the core test. The use of lettering does not indicate a test grade. The letter serves as a quick reference to the

selections made during testing and the considerations required for comparing different groups of data. Option A and B parameter choices are preferred in cases where lab-data must be compared to requirements; however, Option C parameters may need to be used, especially for the evaluation of new technologies.

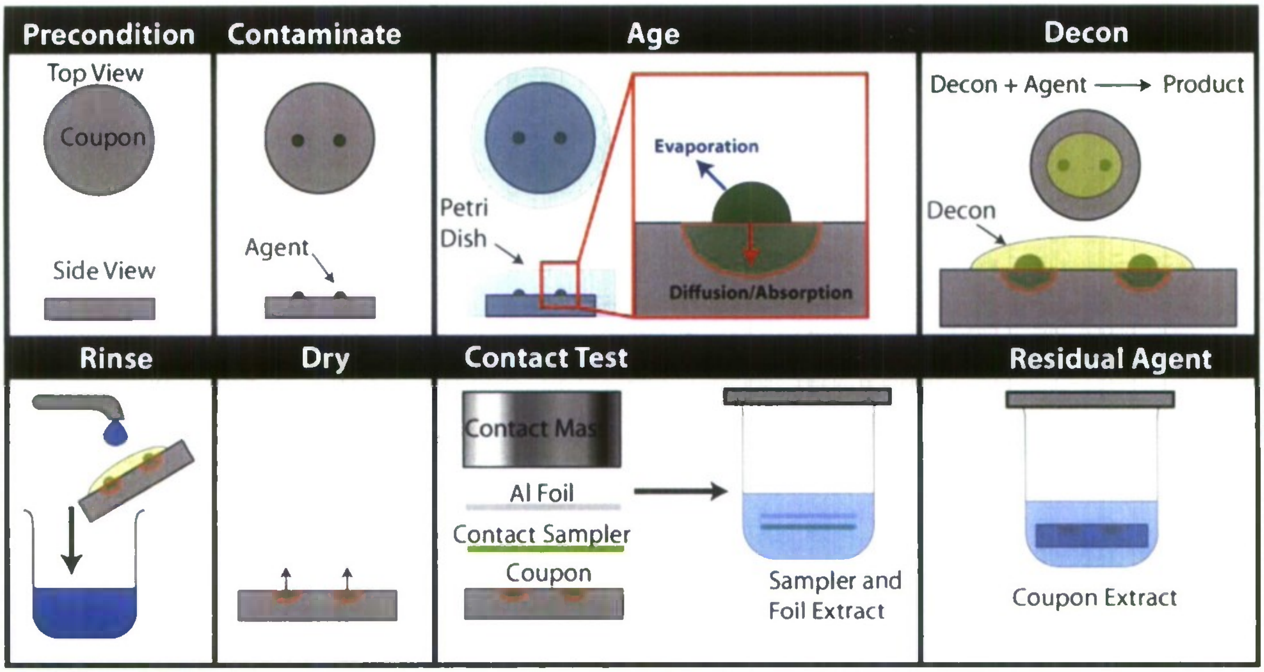

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Figure 6A-1. Contact Test Representation.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- **Identify the calculation desired: contact-hazard, percent neutralization, percent efficacy, or reduction in starting challenge. Review the Calculation Method 6-G and select the appropriate test methods and options within a test method to ensure the necessary data is collected.**
- Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars) and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Prepare decontaminant.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- Recommended that contaminant equilibrate to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case it is important that each coupon is treated identically. The use of timing charts

staggering contamination, decontamination, rinse and contact test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of 5 coupons per test condition and 3 dose-confirmation samples per contamination set.

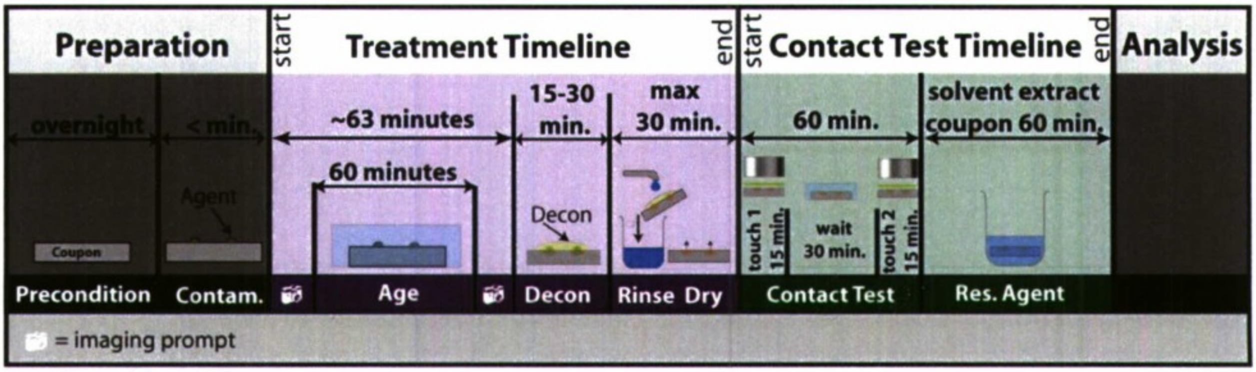

Figure 6A-2. Contact Test Timeline Representation for Option A.

2.0 Precondition Coupons

2.1 Set the environmental chamber to the specified test condition

OPTION A (core test): **moderate condition** test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported.

OPTION B (core test, variable condition): variable condition test with environmental chamber using test sponsor / director temperature and relative humidity set-point. Most common test cases are high and low temperature and relative humidity.

OPTION C (outside core test): test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

2.2 Allow environmental chamber to equilibrate at the set-point temperature and relative humidity. The time to reach set-point equilibration may vary based on equipment and set-point conditions. It is recommended that temperature and humidity are maintained at the set-point for at least 30 min. prior to the start of conditioning.

2.3 The coupons are placed horizontally on coupon trays with the test surface to be contaminated / decontaminated facing upwards.

2.4 Once the chamber has equilibrated at the set-point temperature and relative humidity, place the trays into the environmental chamber for at least 60 min. The recommended practice, if possible, is to precondition the test materials overnight.

- Note: Some materials may require special preconditioning treatments. For example, cellulose based materials and concrete contain significant moisture. These types of materials do not typically achieve moisture equilibrium in less than 24 to 48 hours. Longer precondition times may be required for certain materials. An example procedure for wood is ASTM D4442.

2.5 Samples should not be removed until ready to execute Step 3, Contaminate Coupons.

2.6 Complete the required reporting for this section

3.0 Contaminate Coupons

3.1 Identify contamination density to include number of drops, drop volume and deposition pattern.

OPTION A (core test): contamination density is 1-1.2 g/m^2 applied using pipette / syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): variable contamination density is typically between 1 to 10 g/m^2 applied using pipette / syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

OPTION C (outside core test): application of agent using brushes, rollers, or spray applicators such that the amount of agent applied to the specific surface is not tightly quantifiable. Note: calculation of percent neutralization might not be feasible using this option.

3.2 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with clean, appropriate pipette tip

3.4 Load contaminant delivery tool in accordance with manufacturer's directions.

3.5 Deliver to the surface the appropriate number of drops to achieve the contamination density. Reload the tool and repeat as needed for the total number of coupons. Treatment time starts after the coupon is contaminated. Use of timing charts for multiple samples is recommended.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests) or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.6 If using pipettes or syringes to deliver contaminant, prepare the "dose confirmation" sample. At least three replicate samples are recommended.

3.6.1 Deliver to a scintillation vial the appropriate number of drops to achieve the contamination density.

3.6.2 Add 20 mL of extraction solvent.

3.6.3 Cap vial

3.6.4 Thoroughly mix contents by inverting vial three times.

3.6.5 Using a clean, disposable pipette, load the analytical vial with an aliquot of extractant solution.

3.7 Observe the post-contamination drop interaction with the surface and surface coverage.

OPTION A (core test): Using a digital camera or imaging station, photograph each coupon surface.

OPTION B (core test variable condition): Some materials may not allow for rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three independent coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered should be documented both in words and hand drawing.

3.8 Cover coupons with a Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

3.9 Complete the required reporting for this section.

4.0 Coupon Aging

4.1 Coupons are aged.

OPTION A (core test): Coupons are aged in environmental chamber for 60 min at a moderate condition test with environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. Environmental chamber should have logging capability for real-time temperature and humidity recording.

OPTION B (core test, variable condition): Coupons are aged in an environmental chamber under one or more of the following cases. The environmental chamber should have logging capability for real-time temperature and humidity recording.

- Variable temperature and relative humidity: aging conducted at test sponsor / director designated temperature and relative humidity.
- Variable aging time: shorter aging time for immediate or operational decon applications, or aging period longer than the Option A basic thorough test. The aging may be at the moderate condition and/or variable temperature and relative humidity.

OPTION C (outside core test): Test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

4.2 Observe the post-aging drop interaction with the surface and surface coverage. (If no aging period is used, this step can be skipped).

OPTION A (core test): Using digital camera or imaging station, photograph each coupon surface. There is a chance for some materials the post aging image may not be visible without use of color indicator or dye.

OPTION B (core test variable condition): Some materials may not allow for rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered should be documented both in words and hand drawing.

4.3 Complete the required reporting for this section.

4.4 Coupons are moved to decontamination test area at the end of aging period.

5.0 Pre-rinse the Coupons

5.1 Coupons are rinsed.

OPTION A (core test): pre-rinse is not used for the core test.

OPTION B (core test variable condition): Pre-rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in a glass jar for process and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION C (outside core test): The use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time, hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement.

5.2 Complete the required reporting for this section.

6.0 Decontaminate the Coupons

6.1 Apply decontaminant

OPTION A (core test): For the core test there are a few sub-options based on the test objective. The decontaminants are liquid-phase and applied using a pipette. Dispensettes or pumps may fall under Option A if the decontaminant delivery volume to the contaminated region can be accurately measured. Unless otherwise specified, the decontaminant applied is typically at room conditions. The amount of decontaminant applied is based on the following guidance.

- Option A-1: For early research tests, it is recommended that 1.00 mL of decontaminant is evenly dispensed over the contaminated coupon surface in a single application. Care should be taken to ensure that the decontaminant is delivered uniformly over the test area. This recommended decontaminant volume is for starting challenges in the 1 to 10 g/m^2 range to ensure that decontaminant covers the contaminated surface area. Some agent-material interactions could result in significant contaminated surface coverage that smaller decontaminant volumes may not be able to adequately cover the entire contaminated surface yielding data scatter due to decontaminant delivery.
- Option A-2: FM 3-11.5 recommends a decontaminant to contaminant ratio of 50:1. This corresponds to 0.100 mL to 1.000 mL for a 1 to 10 g/m^2 starting challenge, respectively.

OPTION B (core test variable condition): Some liquid-phase decontaminants may require applying more or less decontaminant. For vapor-phase decontaminants, apply the appropriate fumigant concentration.

OPTION C (outside core test): The use of solid decontaminants, sorbent wipes, brushing or mechanical scrubbing methods are outside the scope. These materials have the potential to retain or physically relocate agent. The use of these methods requires adjustment to calculate percent neutralization. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes fall here.

Decontaminant is applied as best as possible in accordance with technology operating procedures.

6.2 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

6.3 Wait the appropriate decontaminant residence time at the specified environmental conditions.

OPTION A (core test): Standard decontaminant residence time is from 15 to 30 min for liquid-phase decontaminants in an environmental chamber at ambient condition test with environmental chamber using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. Environmental chamber should have charting capability for real-time temperature and humidity logging.

OPTION B (core test variable condition): Liquid-phase decontaminants outside the 15 to 30 minute range or at variable temperature or humidity that are placed in environmental chamber for the residence period.

OPTION C (outside core test): Liquid phase decontaminants evaluated at room condition. Sorbents and wipes may have other residence times on the surface. Vapor-phase decontaminants may dictate environmental conditions as part of the process. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes using residence times outside the core 15 to 30 min or environmental conditions outside specified test conditions fall here.

6.4 Complete the required reporting for this section.

7.0 Post-Rinse and Dry

7.1 Coupons are rinsed.

OPTION A (core test): Rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in a glass jar for processing and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION B (core test variable condition): Rinse is not collected or analyzed.

OPTION C (outside core test): The use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time, hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement. Some decontaminants do not require a post rinse. The impact of residual decon on the contact test analytical measurements must be evaluated.

7.2 Coupon drying

OPTION A (core test): Passive drying is recommended at room conditions, preferably in a chemical fume hood (or equivalent) with approximately 100 linear feet per minute (lfm) airflow. The coupons are recommended to be placed at and angle to increase air flow over surface. Coupons should not be dried for more than 30 min. Any residual water on

the surface should be noted. For most applications, wicking the last bead of rinse water should have little impact on the results.

OPTION B (core test variable condition): Controlled air drying which is active blowing with established air temperature, flow rate, etc.

OPTION C (outside core test): Blotting, wiping, or other direct surface contact methods that may also remove agent as part of the process. These methods can impact contact measurement. No drying would also fall here as residual water affects the contact measurement if trying to conduct the dry-skin equivalent contact test.

7.3 Complete the required reporting for this section.

7.4 The coupon treatment process is considered complete once the surface of interest has dried or the 30 minute dry time has elapsed. The contact test time is initiated as shown in Figure 6A-3.

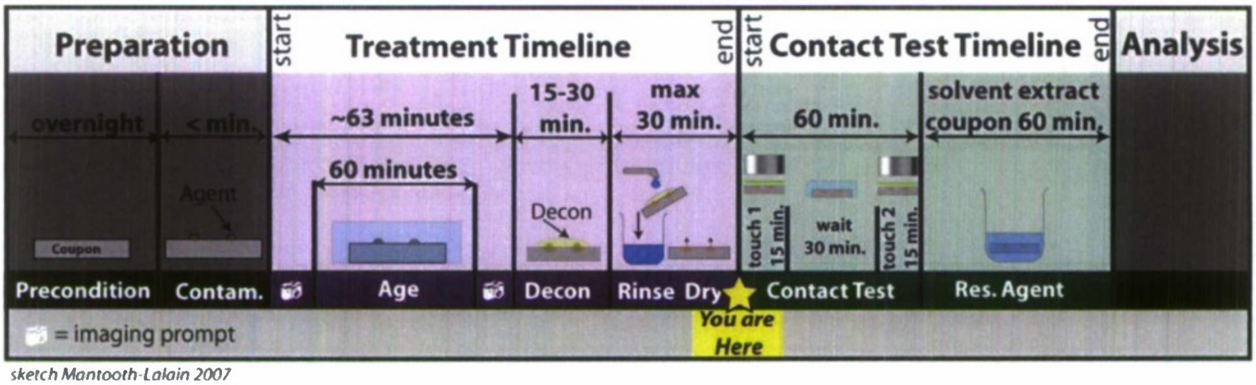

Figure 6A-3. Contact Test Timeline Representation for Option A.

8.0 Contact Test

8.1 A contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). The contact test is the process of applying the contact sampler to the coupon surface for a specified duration of time. The number of contact sampling periods is referred to as "touches."

8.2 Conduct first touch

8.2.1 Place the coupon on the temperature controlled surface set to 30 ± 5 °C (86 ± 9 °F) is preferred. The value should be within ± 10 °C. If the value is greater than ± 10 °C, this must be clearly reported.

8.2.2 Place the contact sampler on the coupon surface.

8.2.3 Place a 2 in. diameter circular piece of aluminum foil on the contact sampler. The aluminum foil is to prevent contaminant breakthrough to the contact mass. .

8.2.4 For uneven or rough surfaces, place a thin foam layer on the aluminum foil.

8.2.5 Place a contact mass onto the foam / aluminum foil layer.

8.2.6 Wait contact time.

OPTION A (core test): the first touch is 15 min in length occurring immediately after decontamination (dry step 7.4) is completed.

OPTION B (core test variable condition): sampling period 15 min in length occurring at a different time point post end of decontamination.

OPTION C (outside core test): a sampling period other than 15 min.

8.2.7 At the end of the sampling period, the contact mass and foam (if used) are removed.

8.2.8 Place the contact sampler and aluminum into a scintillation vial (or equivalent glass container). The aluminum foil is extracted with the contact sampler to ensure any breakthrough mass is collected

8.2.9 Cover coupon with Petri dish to minimize cross contamination and evaporative loss.

8.2.10 Add 20.0 mL of extraction solvent.

8.2.11 Place PTFE/ Teflon-lined lid on extraction scintillation vial.

8.2.12 Thoroughly mix contents by inverting vial three times .

8.2.13 Contact sampler / aluminum will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Method 6-B must use the same extraction time.

8.2.14 At the end of the extraction period, thoroughly mix contents by inverting vial three times.

8.2.15 Using a clean pipette, place a sample into an analytical vial for analysis.

8.3 For Core test, wait 30 min. If no other touches are to be performed, skip to step 8.5.

8.4 Conduct second touch.

OPTION A (core test): The first touch typically has large data scatter, this second touch is recommended for completeness. The process is the same as Step 8.2, if conducted.

OPTION B (core test variable condition): Second touch is skipped and proceeds directly to residual agent measurement.

OPTION C (outside core test): additional sampling periods beyond the first touch, as directed by the test sponsor / director.

8.5 After the last touch is complete, the coupon will be extracted for residual agent.

8.5.1 Place the coupon in an extraction jar. For most materials the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

8.5.2 Add 20.0 mL of extraction solvent ensuring coupon is completely immersed.

8.5.3 Place PTFE/ Teflon-lined lid on extraction jar.

8.5.4 Swirl jar.

8.5.5 Coupon will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Method 6-B must use the same extraction time.

8.5.6 At the end of the coupon extraction period, swirl jar, open vial, and, using a clean pipette tip, place a sample into an analytical vial for analysis.

8.6 Complete the required reporting for this section.

8.7 The contact test is complete.

9.0 Chromatographic Analysis for Agent

9.1 Samples are analyzed based on guidance in Procedure 6-H. This test generates three types of samples for analysis.

- Dose confirmation.
- Contact sampler extract for contact test.
- Coupon extract for residual agent.

9.2 Sample dilution may be required for sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

9.3 Obtain list of analytical results in ng/mL which already accounts any additional dilutions.

9.4 Complete the required reporting for this section.

10.0 Perform Calculations

10.1 Obtain the analytical results for

- Dose confirmation
- Contact sampler extract for contact test
- Coupon extract for residual agent

10.2 Perform calculations.

10.3 Complete the required reporting for this section.

CALCULATIONS – Contact Test Mass

1.0 Convert Results from ng/mL to ng

1.1 Obtain the chromatography data in ng/mL for the contact sampler extract (**CS_E**), the residual agent extract (**RE_E**), and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.

1.2 Convert the contact test result from mass in solution (**CS_E**) to mass (**CS_M**)

For each contact sampler extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{CS_M} \text{ (in ng)} = \mathbf{CS_E} \times \mathbf{EV} \qquad (1)$$

1.3 Convert the residual agent test result from mass in solution (**RE_E**) to mass (**RE_M**)

For each residual agent extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{RE_M} \text{ (in ng)} = \mathbf{RE_E} \times \mathbf{EV} \qquad (2)$$

1.4 Calculate 'Analyte Mass Delivered' ***Del*** from dose confirmation sample

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL. Average results for replicates, reporting relative standard deviation.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (3)$$

2.0 Calculate the Contact Test Results Corrected for Extraction Efficiency

2.1 Obtain the calibration curve developed from Procedure 6-B.

2.2 Calculate the extraction efficiency corrected contact test result (**CS_C**) in nanograms using the equation identified in step 4.0 of procedure 6-B.

3.0 Calculate the Residual Agent Results Corrected for Extraction Efficiency

3.1 Obtain the calibration curve developed from Procedure 6-F.

3.2 Calculate the extraction efficiency corrected residual agent test result (**RE_C**) in nanograms using the equation identified in step 4.0 of procedure 6-F.

4.0 Complete the Required Reporting for this Section

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Decontaminants:** Provide for each decontaminant used the decontaminant name / description, source, date of preparation, purchase or expiration date (as applicable). Include a description of the preparation process for materials requiring pre-use preparation such as dilution or mixing.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.
- **Water:** Provide a description of the water used and source for each use of water. For example, laboratory distilled water may have been used to mix the decontaminant and certified ocean seawater might have been used for the rinse. The water reporting would include the description for both the decontaminant prepared and rinse waters used. Include characterization data / specification sheet details for any certified or specialty water used.

EQUIPMENT

- **Contaminant Delivery Tool**
  - Tool identification including manufacturer, model number, and volume dispensing range.
  - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
  - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
  - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Decontaminant Delivery Tool**
  - *See contaminant delivery tool listing for pipettes and syringes.*
  - For breadboard, brassboard, and prototype equipment, provide a description of the decontamination system including configuration and identification number / name.
  - For vendor provided equipment, provide the vendor name, item description, and model number.
- **Water Rinse Delivery Tool:** *see contaminant delivery tool listing.*
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Temperature Controlled Surface for Contact Test**: include tool identification including manufacturer and model number, and tool performance specifications if available.
- **Environmental Chamber:** Provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems. If a data logger is used, then include the data logging frequency.
- **Contaminated Area Measurement (if performed)**: include tool identification including manufacturer and model number, camera resolution, description of area measurement calculation and associated error with calculation if known.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Contact mass:** description including size, shape, material, and weight.
- **Contact sampler:** include the source, description, part number, lot, and any preparation or treatment (i.e., washing) performed.

- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Precondition Coupons**
  - Option used (A, B or C)
    - For Option C: a description of how the conditioning was performed.
  - Precondition length of time with units of hours and minutes.
  - Temperature average with standard deviation, high, and low for conditioning period.
  - Relative humidity average with standard deviation, high, and low for conditioning period.
  - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (μL) per coupon.
  - Agent drop volume size(s) in microliters (μL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (μL) per vial, the agent drop volume size(s) in microliters (μL) per vial, the solvent identification, and the solvent volume.
- **Post-Contamination Surface Contamination Observation**
  - Option used (A, B or C)
  - Written description of applied drops as they appear for each coupon (e.g., sessile, spread).
  - For Option B: how contrasting was achieved.
  - For Option A/B: provide a representative photograph
  - For Option A/B: provide the calculated contaminated surface area
  - For Option C: provide a hand drawing of the representative contaminated area, estimated contaminated surface area, and the method for estimating contaminated surface area.

- **Aging**
    - Option used (A, B or C)
        - For Option C: a description of how the aging was performed.
    - Coupon cover description including source, part number, size, and volume.
    - Aging length of time in units of minutes.
    - Temperature average with standard deviation, high, and low for aging period.
    - Relative humidity average with standard deviation, high, and low for aging period.
    - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Post-Aging Surface Contamination Observation:** *see requirements for Post-Contamination Surface Contamination Observation.*
- **Pre-Rinse**
    - Option used (A, B or C)
        - For Option C: a description of how rinsing was performed.
    - Rinse material identification (i.e., distilled water, hot soapy tap water, etc.).
    - Rinse material temperature
    - Test location temperature and relative humidity during rinsing.
    - Total volume applied
    - Description of the force and rate rinse applied
- **Decontamination**
    - Option used (A, B or C)
        - For Option C: a description of the decontamination process.
    - Description of the decontaminant application process.
    - Decontaminant temperature.
    - If decontaminant is applied "cold" or "warm" provide a description of how decontaminant was chilled or warmed.
    - Record amount of decontaminant applied
        - For liquids, volume delivered
        - For solids, mass delivered
        - For vapors, injection rate, flow rate, fumigant concentration, temperature, and relative humidity
        - Or other specifications per manufacturer's delivery instructions.
    - Coupon cover description including source, part number, size, and volume.
    - Decon residence time on coupon surface in minutes
- **Post-Rinse:** see *requirements for Pre-Rinse.*
- **Drying**
    - Option used (A, B or C)
        - For Options A, B and C: a description of how drying was performed.
        - For Option C: if no drying was used, provide a detailed description of how wet the surface was (representative photograph recommended).
    - Drying time in minutes
    - Description of drying location
        - If hood, specify air velocity
        - If flow chamber, specify flow rate and air temperature.
    - Temperature
    - Relative humidity
    - Description of any residual water on surface at the end of the drying period.
    - Detailed description of drying process used.
- **Contact Test:** for each touch provide:
    - Temperature of controlled surface
    - Touch number
    - Contact sampling period in minutes

- Time contact sampling period occurred post-decontamination. For example, a 15 minute contact sampling period started at 45 minutes and ending at 60 minutes post decontamination.
- Extraction solvent
- Extraction time

- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the contact test results in nanograms per coupon, "dose confirmation" sample mass in nanograms and residual agent coupon results in nanograms per coupon.
- **Calculation Reporting Criteria**
  - Summary data table containing the following information. Some data may not be available based on procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
    - Data in ng/mL for the contract sampler extract (**CS_E**), the residual agent extract (**RE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
    - Contact test mass results (**CS_M**), not corrected for extraction efficiency in ng.
    - Residual agent mass results (**RE_M**), not corrected for extraction efficiency in ng.
    - Delivered mass results (***Del***) in ng.
    - Extraction efficiency corrected contact test mass results (**CS_C**) in ng.
    - Extraction efficiency corrected residual agent mass results (**RE_C**) in ng.
    - Test set (combination of test replicates) averages and standard deviations for data sets specific to reporting results for test objective(s).
  - Summary of the contact sampler extraction efficiency determination (Procedure 6-B) for each contaminant -extraction solvent pair if Procedure 6-B was not directly executed and reported for this test report.
    - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
  - Summary of the coupon extraction efficiency determination (Procedure 6-F) for each agent – material - extraction solvent combination if Procedure 6-F was not directly executed and reported for this test report.
    - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
  - Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a

test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the Amount of Contaminant Delivered in order to determine the difference. The Amount of Contaminant Delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Aging Temperature and Relative Humidity: Core test moderate condition is 21 ± 3 °C, preferred, ± 5 °C maximum. Aging temperature in general is target temperature ± 5 °C. No criterion for RH is specified, however, a test sponsor may specify depending on test objective.

- Rationale: Changes in temperature directly affect the amount of contaminant absorbed into a material. Any deviation in temperature increases the amount of error in the end test result. Therefore, deviations in temperature must be minimized. For example, mass transport coefficients typically double for every 10 °C increase in temperature.
- Rationale: Relative humidity is expected to have a minor influence on test results compared to other system variables.

Aging Time: Core test aging time is 60 ± 3 min. For other aging times, the acceptance criterion is target time ± 5%.

- Rationale: The more or less time a contaminated coupon is aged, the more or less contaminant is absorbed into the coupon. For example, mass adsorbed for sorptive non-porous materials (based on Fick's first law) is proportional to square root of the aging time. A 5% time deviation could result in a 2.5% variation in mass absorbed into the coupon.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Amount of Decontaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered. In the event these criteria were not met, a repeatability study could be performed to determine the precision of the tool.

Decontaminant Residence Time: The total decontaminant residence time should be within ± 5% target time.

- Rationale: The measurement of the effect the decontaminant has for contaminant reduction is the main objective of the test. The decontaminant–contaminant interaction time will be proportional to the amount of agent removed and or neutralized, likely in a nonlinear manner.

Contaminated Surface Area (Contact): The contaminated surface area for a test set should have a small variance, although contaminant spreading on a material surface is a function of material-agent interactions. A large variance in the contaminated surface area could give false sense of test error; the cause of the variability should be investigated to determine if the data is acceptable. It is recommended to investigate if the variance in spreading is a property of the material-agent interactions or if it was a result of test procedures. If it was a result of test procedures the test should be rerun.

- Rationale: For sorptive materials the mass absorbed is proportional to the contaminated surface area (absorption is a flux-based process).
- Rational: For the contact test result, the agent mass sampled will be proportional to the contaminated surface area. The proportionality (e.g., square root area, linear area, area squared) is dependent on material properties and agent-material interactions.
- Note: The contaminated surface area immediately after contamination is likely to have little variation, however some material-agent combinations will result in spreading as a function of time, thus the pre-decon contaminated area may show a significant distribution. The pre-decon contaminated area should be used as the value to compare contaminated surface areas.
- Note: For comparison of data with different contaminated surface areas it is recommended to compare data using a mass per unit of contaminated surface area value rather than direct mass comparisons.

Contact Test Temperature: The contact test surface and contact masses temperature is 30 ± 5 °C (86 ± 9 °F).

- Rationale: This temperature is to represent the temperature of an extremity (e.g., hand) which is less than the core body temperature of 37 °C.

- Rationale: Mass transport coefficients typically double for every 10 °C. Temperature changes directly affect mass absorption into the contact sampler.
- Rationale: Contact masses may have significant thermal mass. Conducting tests without preheating masses may result in an inaccurate contact test temperature and variable mass absorption.

Contact Test Touch Time: The core contact test touch time is 15 minutes ± 45 seconds. If other touch durations are used the contact test touch time should be within ± 5% of the target total touch time.

- Rationale: The contact test result will vary with the contaminated surface area and touch length of time. For non-sorptive surfaces, the majority of mass adsorbed by the contact sampler is likely to occur within the first minute and is less affected by time. The contact touch time duration is directly proportional to contact test result for sorptive surfaces.

Contact Test Pressure: The core test contact test pressure is 0.7-1.0 psi (0.05-0.07 kg/cm^2), unless specified differently by test sponsor.

- Rationale: The pressure exerted on the contact sampler will determine the degree of contact between the contact sampler and the coupon. The contact sampler is usually a 'soft' material (i.e., low durometer) and will deform when pressure is applied. When more pressure is applied, the contact sampler will deform and increase the microscopic contact area due to 'filling in' the microscopic surface roughness of the sample and contact sampler. Increasing the pressure will increase the contact area which will increase mass absorption in the contact sampler. This has been documented in work by Schwope.
- Note: contact condition (wet vs. dry) has the same effect. If the coupon is wet, the water will 'fill in' the microscopic surface roughness and result in an increase in mass absorption in the contact sampler and may alter mass transport mechanisms.

Contact Sampler: The contact sampler is a simulant for human skin. The only guidance for material selection at this time is latex dental dam. The comparison of data using different contact sampler material may not produce similar results limiting direct comparison of test data.

- Rationale: The contact test is supposed to measure the mass of agent that would be transferred to skin. The mass of agent transferred to the contact sampler is a function of mass transport phenomenon that are material dependent (see EPA/600/8-91/011B 1992, *Dermal Exposure Assessment: Principles and Applications*). Materials with different mass transport properties will yield different mass absorption results. Comparison of contact results using different contact sampler materials is not advised.
- Note: the absorption rate of a contact sampler (skin or latex) is specific to the transport properties of the contaminated material, agent, and contact material. There is the possibility that skin and latex may have similar absorption rates on one material, but not on another.
- Note: The use of dental dam is recommended, though there is currently no published report characterizing the difference between this material and skin transport from various materials.

REVISION HISTORY

March 2008: original document in source document format. Based on TOP 8-2-061, 2002 initial release.

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Test Procedure 6-B: Contact Sampler Test Methods – (I) Extraction Efficiency and (II) Transfer Efficiency

SUMMARY OF PROCEDURE

The contact sampler extraction efficiency test method (Procedure I) determines the amount of agent that can be recovered from the contact sampler using a specific solvent and extraction time. The mass of agent recovered is compared to the mass originally delivered to enable correction of analytical data based on solvent extraction efficiency for a given extraction time. Any loss in the system, such as evaporation, will contribute to lowering the measured extraction efficiency value. Dose-confirmation samples are used to measure the delivered mass. The delivered mass must be accurately measured to calculate the extraction efficiency. The test covers a range of concentrations equivalent to 250 mg/m^2 through **requirement levels**, which at the time of writing are approximately as low as 0.005 mg/m^2. These results are used to correct the reported residual agent mass value reported in Procedures 6-A and 6-D.

The **contact sampler transfer efficiency** test method (Procedure II) is the ideal case assessment of the ability of the contact sampler to collect available agent from a nonsorptive surface. This method provides guidance for the identification and evaluation of the material used as a contact sampler. This procedure calculates the percent of mass that was delivered to a coupon and transferred to a contact sampler, as a variable called Transfer Efficiency (TE). This TE should not be used to correct data. The TE provides one way to compare different materials used as contact samplers. TE may be specific to coupon material-agent-contact sampler combinations

These procedures provide the following information:

- Contact sampler extraction efficiency method (Procedure I) provides an extraction efficiency calibration curve for the correction of agent mass reported as a function of the solvent extraction efficiency for a given extraction time.
- This method should be performed when any major changed is made in the laboratory process. Major changes include, new material lot, change in extraction procedure (e.g., time, temperature, extraction volume), change in solvent (e.g., different solvent or change in solvent grade used).
- Contact sampler transfer efficiency test method (Procedure II) provides guidance for the identification and evaluation of the material used as a contact sampler

The following prerequisite tests are required for this test procedure:

- Procedure 6-H, "Chromatographic Analysis Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

Limitations:

- For ultra-low dose levels, non-detect recovery masses may be observed giving the appearance of a low-extraction efficiency. The calculations account for this situation.
- An assumption of this procedure is that all mass lost is attributed to incomplete extraction. Care should be taken in executing the method to ensure minimal agent loss occurs due to evaporation (especially for more volatile compounds) and coupon handling.
- The extraction efficiency calibration curve should only be used for the contamination drop volume and deposition pattern tested for an agent–material–solvent combination. If other drop volumes, deposition patterns, or solvents are

routinely used for an agent-material pair, then the extraction efficiency calibration curve should be generated for each variable set (e.g., drop volume, deposition pattern, agent, material, and solvent combination).

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA). In this case, the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample** - liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **bioavailable** – in toxicology, the degree to which a substance becomes available to the target tissue after administration of a defined exposure. In regard to the contact test, the contaminant mass transferred to the contact sampler that could be biologically available under appropriate conditions.
- **chemical agent** - is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contact mass** - a uniform mass used to apply pressure during the contact test. The masses are typically prepared from stainless steel. The masses should evenly exert 0.7-1.0 psi (0.05 to 0.07 kg/cm^2) pressure on the coupon surface. For the 2 in. diameter disk, this is equivalent to a 2 in. diameter cylindrical mass weighing 1 kg.
- **contact sampler** - material used in this contact test as a surrogate for human skin. The sampler sorbs the available surface contamination which is then extracted to determine the mass of agent potentially bioavailable or available for contact transfer.
- **contact sampler transfer efficiency** - the measurement of the contact sampler's ability to collect the contaminant from the test material (e.g., coupon). More specifically, the contact sampler's ability to sorb the analyte under the ideal case by using a nonsorptive material. Transfer efficiency may be different for material-agent combinations.
- **contact transfer** - the capability for a contaminant present on a specific surface to be moved to another through touching the contaminated surface.
- **contaminant** - a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical, and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination** - the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)

- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – a sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency -** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*
- **moderate condition -** test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization -** the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials -** a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **panel** – *see coupon.*
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.

- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface it is better described as a thin film.
- **skin simulant** – material used in the contact test to estimate the contaminant transfer that may occur if the surface of interest was contacted (e.g., touched) by real skin. See test limitations regarding use for contact testing.
- **sorptive or porous materials -** a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition -** for a specific agent – material- decon set the combined contamination, aging, decontaminant process, environmental, and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **touch -** a contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). For the coupon test, the contact area is nominally the coupon area. The pressure is 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure which is equivalent to a 1 kg contact mass that is cylindrical with a 2 in. diameter. The contact time is typically 15 min.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.9, Potential Military Chemical/Biological Agents and Compounds, 10 January 2005.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
  - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."

- Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
- Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.

- **Extraction solvents:** The test requires the extraction of sorbed agent from test materials such as the contact sampler and/or coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride, and solvent blends.

EQUIPMENT

The equipment required for this method includes tools for delivering contaminant, maintaining environmental control and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (μL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 μL delivered as two 1 μL drops for a 1 g/m^2 starting challenge.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. Also best suited for pipetting volatile liquids. The smallest delivery volume, based on survey of commercial items with repeater capability, is about 1 μL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.

- Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. Smallest delivery volume based on survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
- Computerized Dispensing System: Automated tool with the ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.

- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
  - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.
- **Temperature Controlled Surface for Contact Test:** The lab-scale testing uses a temperature controlled surface to mimic body temperature regulated at 30 ± 5 °C (86 ± 9 °F). The value should be within ±10 °C. If the value is greater than ± 10 °C, this must be clearly reported.
  - Slidewarmer: temperature controllable surface typically used in histological testing. Tools obtained or developed by the testing laboratory which has no performance specification, standard, or vendor provided

performance information must be tested to determine their accuracy and precision.

- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Method 6-H. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space, protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Contact mass(es):** Laboratory scale contact test utilizes a mass to deliver 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure during the contact touch. For the 2 in. disk, the mass is a stainless steel, 2 in. in diameter cylinder weighing 1 kg placed onto the sample surface for the duration of the contact time.
- **Contact sampler(s):** Adsorptive material used to collect available contamination from surface of interest. The use of latex dental dam, preferably unflavored, uncolored, and heavy gauge is suggested. Testing will typically use 0.01 in. thick material.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the contact sampler and/or coupon. A glass container such as a vial or jar of sufficient size to hold both the contact sampler and/or coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommended for chemical agent testing.
- **Foam**
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** are typically used during the aging step to cover the coupon surface to minimize evaporative loss. Can also be used as sample holder.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks, and writing utensils.

- **Timing device(s):** Test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Transfer pipettes**
- **Optional items:** Items that may be used based include analytical balance.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE I – Contact Sampler Extraction Efficiency

The procedure specifies the sample handling, measurement, and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements. The extraction efficiency function determined by this method is valid for the tested material lot and extraction method used. Lot-to-lot variations in test materials may exist and should be verified.

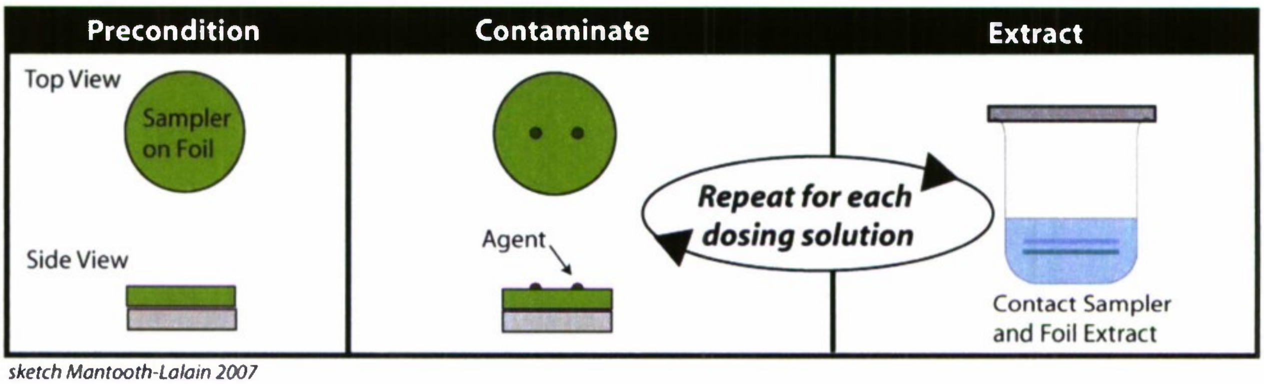


Figure 6B-1. Contact Sampler Extraction Efficiency Test Sketch.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).

- Completion of test area setup, labeling (i.e., vials, trays, jars), and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- Recommended that contaminate equilibrate to room temperature prior to use.

This procedure can be applied to multiple contact samplers during a single test session. In that case it is important that each contact sampler is treated identically. The use of timing charts staggering contamination, decontamination, rinse, and contact test times is strongly encouraged as subtle differences in contact sampler treatment can contribute to data scatter.

The recommended number of replicates is a minimum of 5 contact samplers per test condition and 5 dose-confirmation samples per contamination set.

The test is performed at the conditions at which the extraction will occur.

2.0 Prepare Dosing Solutions

2.1 Up to seven dosing solutions are prepared to provide various delivered mass values. Identify the smallest mass on the surface of the test material (e.g., coupon, dental dam) for the following two situations.

2.1.1 Multiply the smallest requirement surface concentration by the surface area of the test material to calculate the mass on coupon (e.g., JPID 2003 objective for VX is 0.005 mg/m^2 x 0.00202 m^2 x 10^6 ng/mg = 10.1 ng on coupon). Divide the mass on coupon by 10.

$$Mass_{\text{Requirement}} = \frac{\text{Requirement} \cdot \text{Surface Area}}{10} \cdot 10^6$$

2.1.2 The second situation to consider is the detection limit of the analytical method. Multiply the LOQ (ng/mL) of the most sensitive analytical method used (e.g., the LOQ of 0.05 ng/mL for VX on LC-MS/MS) by the extraction volume (mL) as defined by

$$Mass_{\text{Analytical}} = LOQ \cdot Volume_{Extract}$$

2.1.3 The value $Mass_{Min}$ is defined as the smaller of $Mass_{Requirement}$ or $Mass_{Analytical}$.

Note: If $Mass_{Requirement}$ is less than $Mass_{Analytical}$, this implies that the analytical quantitation limit cannot detect an order of magnitude below the requirement.

2.2 Determine the mass of contaminant to deliver to the coupon

2.2.1 The selection of masses to be delivered is based on the fitting of the empirical EE models. The following guidance will deliver a model that should represent the system.

2.2.2 Calculate the mass to be delivered using the following table as guidance

2.2.3 Calculate the concentration of the solution to deliver the same contamination profile as used in testing (e.g., Procedures 6-A, 6-D and/or 6-F) to contaminate the coupon. For example, if two 1.0 µL drops are used to contaminate the coupon with neat agent for testing, use two 1.0

μL drops for this test. Solution concentration (ng/mL) can be calculated from the $Mass_{Delivered}$ (ng), number of drops (n), and drop volume (V in μL) as

$$\text{Sln. Conc} = \frac{Mass_{Delivered}}{nV \cdot 10^{-3}}$$

Guidance Formula	Example: VX $Mass_{Delivered}$ $Mass_{Min}$ = 1.00 ng	Resulting Nominal Solution Conc. (ng/mL) for 2 x 1.0 μL drops
$Mass_{Min}$ × 2	2	1,000
$Mass_{Min}$ × 5	5	2,500
$Mass_{Min}$ × 10	10	5,000
$Mass_{Min}$ × 33	33	16,500
$Mass_{Min}$ × 100	100	50,000
$Mass_{Min}$ × 1,000	1,000	500,000
$Mass_{Min}$ × 10,000	10,000	5,000,000

2.3 Prepare the dosing solutions

2.3.1 The solutions can be prepared either volumetrically or gravimetrically. The discussion here is for volumetric addition. This procedure could be scaled up to use volumetric glassware. The approach here was to reduce total agent consumption and waste generated. An example solution preparation table for VX using an 89.5% pure neat agent is shown. Higher concentration solutions are prepared from neat agent, and then serially diluted to create lower concentration solutions.

Note: Extraction efficiency is determined from mass delivered which is measured by dose-confirmation samples (i.e., not solution concentration x dose volume); this approach minimizes any bias introduced by the dosing tool or solution preparation technique and reduces the accuracy required to prepare the dosing solutions.

2.3.2 The solutions are prepared by the placement of a set volume of solution dispensed via pipette into a vial to which the appropriate volume of solvent is added via pipette.

2.3.3 The vial is immediately capped using a PTFE/Teflon lined cap.

2.3.4 The vial is inverted three times for thorough mixing.

Agent	**VX**
Density (ng/ml)	1,008,300,000
Mole % Purity	89.5%
Corrected Density	902,428,500

Standard Name	Nominal Conc (ng/mL)	Stock Solution	Volume Stock Sln (mL)	Solvent Volume (mL)	Total Vol (mL)	Corrected Conc (ng/mL)
SolutionA	50000000	Neat	0.059	1.000	1.059	50,276,942
SolutionB	5000000	SolutionA	0.112	1.000	1.112	5,063,865
SolutionC	500000	SolutionB	0.110	1.000	1.110	501,824
SolutionD	50000	SolutionC	0.111	1.000	1.111	50,137
SolutionE	16500	SolutionC	0.034	1.000	1.034	16,501
SolutionF	5000	SolutionD	0.112	1.000	1.112	5,050
SolutionG	2500	SolutionD	0.053	1.000	1.053	2,524
SolutionH	1000	SolutionE	0.065	1.000	1.065	1,007

2.4 Complete the required reporting for this section

3.0 Contaminate Contact samplers

3.1 The contact samplers are placed on aluminum foil disks.

3.2 The contamination approach should match that used in the core test Method 6-A. Identify contamination density to include number of drops, drop volume, and deposition pattern. Test Method 6-A Option C cannot be performed for this test as the amount delivered cannot be tightly measured.

OPTION A (core test): contamination density is 1-1.2 g/m^2 applied using a pipette, syringe, or equivalent tool as 1 μL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): variable contamination density is typically between 1 to 10 g/m^2 applied using pipette, syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

3.3 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.4 Fit pipettor with clean appropriate pipette tip

3.5 Load contaminant delivery tool with dosing solution in accordance with manufacturer's directions.

3.5.1 Deliver to the surface the appropriate number of drops to achieve the contamination density.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests), or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.5.2 Allow the solvent to evaporate which is typically 5 to 20 seconds. Do not exceed 60 seconds.

3.5.3 Place the contact sampler and aluminum into a scintillation vial (or equivalent glass container).

3.5.4 Add 20 mL of extraction solvent

3.5.5 Place PTFE/ Teflon-lined lid on extraction scintillation vial.

3.5.6 Thoroughly mix contents by inverting vial three times

3.5.7 Contact sampler / aluminum will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction time used here should agree with extraction time used for testing (e.g., Procedures 6-A, 6-D or 6-E).

3.5.8 Thoroughly mix contents by inverting vial three times

3.5.9 Using a clean, disposable pipette load the analytical vial with an aliquot of extractant solution.

3.5.10 Repeat steps 3.5.1 through 3.5.9 as needed for the total number of contact samplers.

3.5.11 Prepare the "dose confirmation" sample. At least five replicate samples recommended.

3.5.11.1 Deliver to a scintillation vial the sample number of agent drops.

3.5.11.2 Add 20 mL of extraction solvent.

3.5.11.3 Cap vial

3.5.11.4 Thoroughly mix contents by inverting vial three times.

3.5.11.5 Using a clean, disposable pipette, load the analytical vial with aliquot of extractant solution.

3.6 Repeat steps 3.4 and 3.5 for each solution.

3.7 Complete the required reporting for this section.

4.0 Chromatographic Analysis for Agent

4.1 Samples are analyzed based on guidance in Procedure 6-H.

- Dose confirmation
- Contact sampler extract

4.2 Sample dilution may be required for sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

- Note: the dilution process should have as few steps as possible. The dilution process must be documented in final report.

4.3 Obtain list of analytical results in ng/mL which already accounts any additional dilutions beyond initial extraction.

4.4 Report for this section

- Analytical results
    - All of the reporting requirements for Procedure 6-H which include: description of analytical methodology used including use and acceptance for CCV samples, calibrated range, method LOD / LOQ
    - "dose confirmation" sample mass in ng
    - Contact sampler extraction results in ng/coupon.

5.0 Perform Calculations

5.1 Obtain the analytical results for

- Dose confirmation
- Coupon extract

5.2 Perform calculations.

5.3 Complete the required reporting for this section.

CALCULATIONS

1.0 Prepare Results Table

1.1 Obtain the chromatography data in ng/mL for the contact sampler extract (**CS_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis. Due to the dynamic range of the data included in this analysis, several analytical methods may be used to analyze the samples. If there is a sample that reports a non-detection value and there is an analytical method with a lower detection limit, the sample should be re-run on the more sensitive method.

1.2 Calculate 'Analyte Mass Recovered' ***Rec***.

For each contact sampler extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Rec} \text{ (in ng)} = \mathbf{CS_E} \times \mathbf{EV} \qquad (1)$$

- **Note**: Any data that is below the analytical method lower quantitation limit should not be reported or used in the fitting and analysis.

1.3 Calculate 'Analyte Mass Delivered' ***Del***.

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

1.4 Calculate the average and standard deviation of the delivered mass for all replicates of each solution. (Acceptance criteria: the relative standard deviation (std/avg) must be < 15%)

1.5 Prepare results table for each dosing concentration listing the target mass on coupon, delivered and recovered results.

1.6 Calculate the Extraction Efficiency (**EE**) for each sample which is calculated per Equation 3.

$$\mathbf{EE} = \boldsymbol{Rec} \,/\, \boldsymbol{Del} \qquad (3)$$

1.7 Two calibration models will be calculated, the following procedures will identify which calibration curve best represents the extraction performance.

2.0 Prepare the Independent and Relative Recovery (IRR) EE Calibration Curve

2.1 Calculate 1 / **Del** from the average calculated in step 1.4.

2.2 For each replicate sample plot 1 / **Del** vs. **EE** (calculated in step 1.6).

- **Note**: do not calculate an average EE for each dose solution. The empirical fitting uses each **Rec** data point.

2.3 Apply a linear regression to the data.

2.4 The IRR EE calibration curve assumes the following relationship where R is a relative recovery term and I is an independent loss term. The slope obtained from step 2.3 equals -I, R equals the intercept from step 2.3

$$\boldsymbol{Rec = (Del \times R) - I} \qquad (4)$$

$$\mathbf{I} = \text{-slope (of 1/Del vs. EE)}$$

$$\mathbf{R} = \text{intercept (of 1/Del vs. EE)}$$

2.5 Calculate the EE as a function of delivered mass for the calibration curve:

$$\boldsymbol{EE_{IRR}(Del)} = \mathbf{R - I \,/\, Del} \qquad (5)$$

2.6 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = (\mathbf{EE - EE_{IRR}(Del)})\text{^}2 \qquad (6)$$

2.7 Calculate the sum of the square of the errors. This term is used later to select which calibration curve to use.

$$\mathbf{SSE_{IRR}} = \Sigma\sigma^2 \qquad (7)$$

2.8 If this EE calibration curve is chosen, the EE corrected mass is calculated by

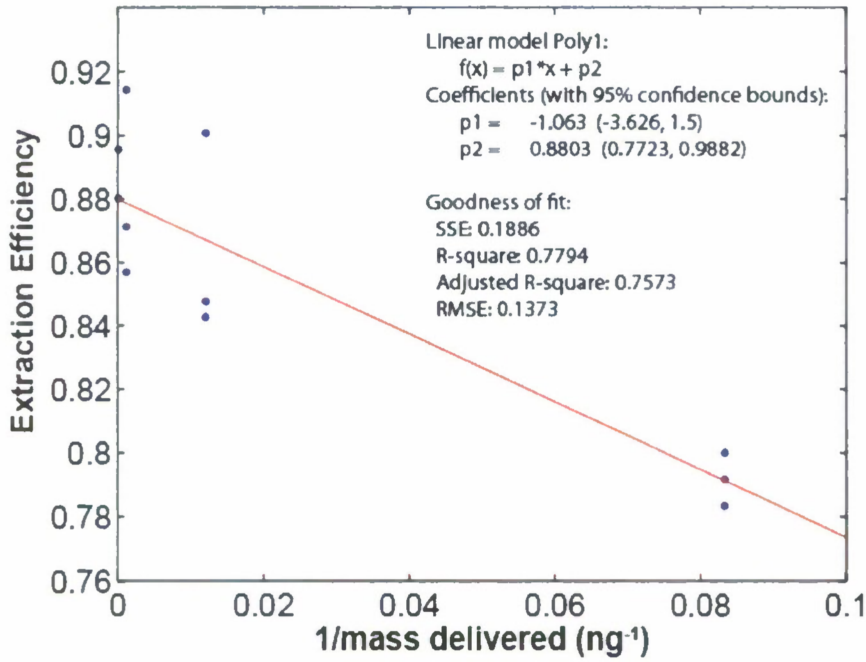
$$\mathbf{Mass_C = (Mass_M + I) \,/\, R} \qquad (8)$$

Note: if the extracted mass (M_E) is below the limit of quantitation (LOQ), the corrected mass should be reported as below quantitation or below detection.

Sample Calculation of Step 2.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	1 / Mass Delivered (ng^{-1})	Mass Recovered (ng)	Extraction Efficiency
15	12.0 ± 1.4 [11.6%]	0.083031	9.6	0.795
			9.4	0.778
			9.5	0.785
100	82.7 ± 2.8 [3.4%]	0.012099	70.1	0.848
			69.7	0.843
			74.5	0.901
1,000	834.3 ± 16.6 [2.0%]	0.001199	726.9	0.871
			715.0	0.857
			762.7	0.914
10,000	8538.8 ± 313.3 [3.7%]	0.000117	7,646.5	0.896
			15,431.8*	1.807*
			7,515.3	0.880

*identified as statistical outlier



Calibration Curve Coefficients:

I = -slope = -p1 = 1.063 (ng)

R = intercept = p2 = 0.8803 (unitless)

3.0 Prepare the Power Law (PL) EE Calibration Curve

3.1 Calculate log (**Del**) from the average calculated in step 1.4.

3.2 Calculate log (**Rec**) for each replicate sample calculated in step 1.2.

3.3 For each replicate sample plot log (**Del**) vs. log (**Rec**). Note: do not calculate an average log (**Rec**) for each dose solution. The empirical fitting uses each individual data point.

3.4 Apply a linear regression to the data.

3.5 The PL calibration curve assumes the following relationship where the slope (m) and intercept (b)

$$\boldsymbol{Rec = 10^{b} \times Del^{m}} \qquad (9)$$

3.6 Calculate the EE as a function of delivered mass for the calibration curve:

$$\boldsymbol{EE_{PL}(Del) = (10^{b} \times Del^{m}) / Del} \qquad (10)$$

3.7 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = (\mathbf{EE - EE_{PL}(Del)})^2 \qquad (11)$$

3.8 Calculate the sum of the square of the errors

$$\mathbf{SSE_{PL} = \Sigma\sigma^2} \qquad (12)$$

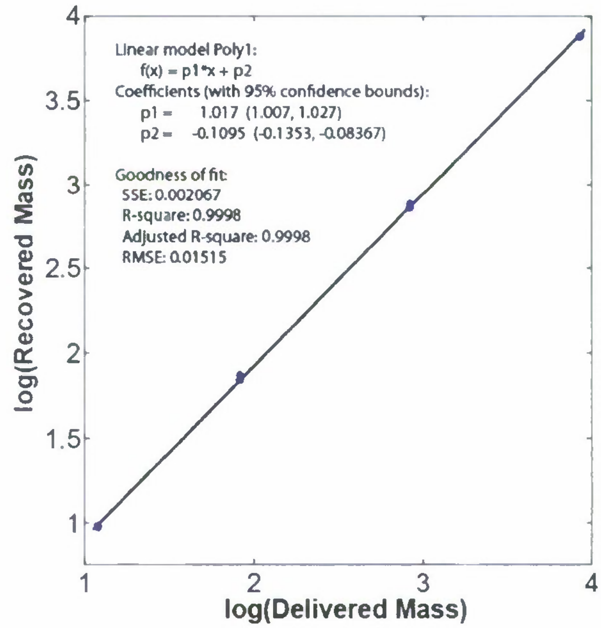
3.9 If this EE calibration curve is chosen, the EE corrected mass is calculated by

$$\mathbf{Mass_C = (Mass_M / 10^{b})^{1/m}} \qquad (13)$$

Sample Calculations of Step 3.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	Log(Del)	Mass Recovered (ng)	Log(Rec)
15	12.0 ± 1.4 [11.6%]	1.079	9.6	0.9809
			9.4	0.9718
			9.5	0.9754
100	82.7 ± 2.8 [3.4%]	1.918	70.1	1.845
			69.7	1.843
			74.5	1.871
1,000	834.3 ± 16.6 [2.0%]	2.921	726.9	2.861
			715.0	2.854
			762.7	2.882
10,000	8538.8 ± 313.3 [3.7%]	3.931	7,646.5	3.883
			15,431.8*	4.188*
			7,515.3	3.875

*identified as statistical outlier



Calibration Curve Coefficients:

m = slope = p1 = 1.017 (unitless)

b = intercept = p2 = -0.1095 (unitless)

4.0 Select the EE Calibration Curve

4.1 Compare the SSE values for each calibration curve. The calibration curve with the smaller SSE provides the better fit.

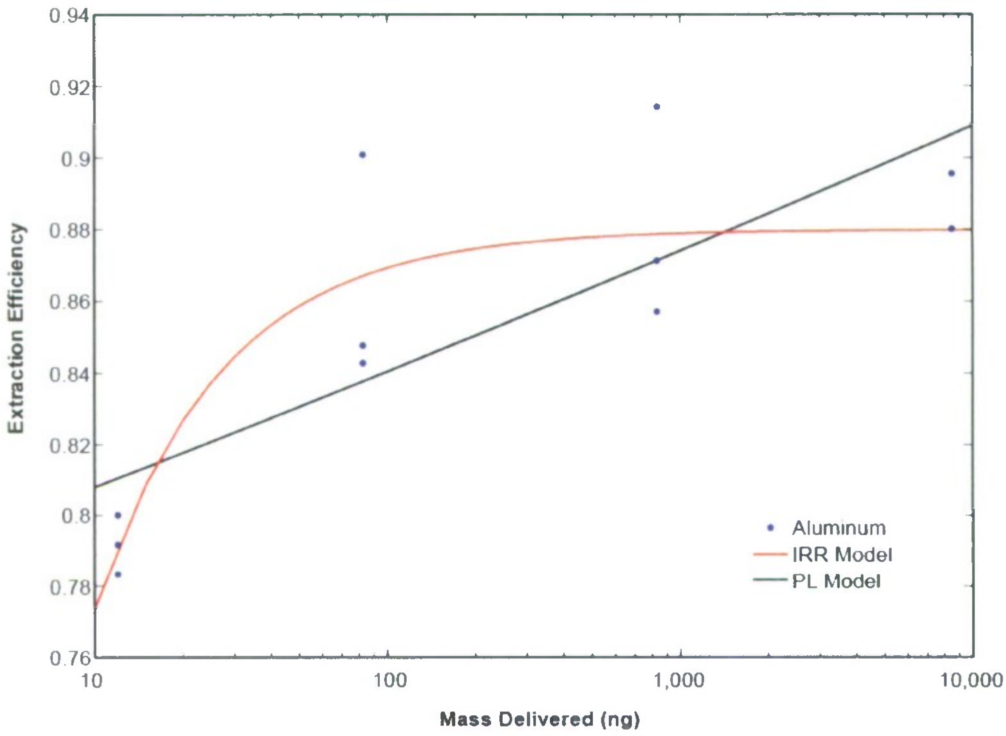
4.2 Plot **Del** vs. **EE**, and **Del** vs. $\mathbf{EE_{Model}}$ **(Del)** to visually confirm the model fits the data.

4.3 For any calculations that use extraction efficiency correction, use Equation 8 if the IRR calibration curve was selected or Equation 13 if the PL calibration curve was selected.

- **Note**: the EE calibration curve has similar 'rules' of implementation as an analytical instrument calibration curve; recovered masses applied to the EE calibration curve that are significantly outside of the tested mass values may not return accurate results.
- **Note:** Extrapolation of the EE calibration curve above the tested range must be handled with caution. Multiple EE calibration curves may be needed to test from contamination density (e.g., 1- to 10 g/m^2) extractions down to requirements (e.g., 0.05 mg/m^2) level extractions. This is especially true for reduction in starting challenge calculations where extracted masses may be large.
- **Note**: Due to the limitations of EE testing caused by evaporation and other loss mechanisms, extrapolation to ranges below the test range qualifier will be allowed at this time.

4.4 Report which EE calibration curve was used and the coefficients used in the calibration.

Mass Del (ng)	Data EE	IRR Model EE	IRR Residual (σ)	IRR σ^2	PL Model EE	PL Residual (σ)	PL $(\sigma)^2$
12.0	0.7947	0.7917	0.0029	8.614E-6	0.8107	-0.0160	2.567E-4
	0.7781		-0.0136	1.842E-4		-0.0325	1.058E-3
	0.7847		-0.0070	4.857E-5		-0.0259	6.722E-4
82.7	0.8480	0.8675	-0.0195	3.789E-4	0.8377	0.0103	1.054E-4
	0.8432		-0.0243	5.893E-4		0.0055	2.974E-5
	0.9009		0.0335	1.119E-3		0.0632	3.992E-3
834.3	0.8713	0.8790	-0.0077	5.933E-5	0.8713	0.0000	1.474E-9
	0.8570		-0.0220	4.840E-4		-0.0143	2.033E-4
	0.9142		0.0352	1.238E-3		0.0429	1.843E-3
8538.8	0.8955	0.8802	0.0153	2.350E-4	0.9064	-0.0109	1.193E-4
	1.807*		N/A	N/A		N/A	N/A
	0.8801		0.0000	1.295E-9		-0.0263	6.911E-4
Goodness of Fit			**SSE**	**0.00435**		**SSE**	**0.00897**
			RMSE	**0.01988**		**RMSE**	**0.02856**
			$\mathbf{R^2}$	**0.8151**		$\mathbf{R^2}$	**0.6057**
			Corr. Coef.	**0.9028**		**Corr. Coef.**	**0.7783**



TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.

EQUIPMENT

- **Contaminant Delivery Tool**
  - Tool identification including manufacturer, model number, and volume dispensing range.

- Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
- Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
- For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.

- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Contact sampler:** include the source, description, part number, lot, and any preparation or treatment (i.e., washing) performed.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Dosing Solution Preparation**: include the number of dosing points, list of target delivered mass per test surface (e.g., coupon, contact sampler) in nanograms, corresponding list of nominal solution concentrations in nanograms per milliliter, and a description of dosing solutions preparation
- **Contamination**
    - Option used (A, B or C)
        - For Option C: a description of how the contamination was performed.
    - Contamination density in g/m^2.
    - Total agent volume in microliters (μL) per coupon.
    - Agent drop volume size(s) in microliters (μL) per coupon.
    - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
    - Test location temperature and relative humidity during contamination.
    - Contaminant temperature at time of contamination.
    - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Contact Sampler Extraction:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting

and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the contact sampler extraction results in nanograms per contact sampler and dosing solution sample mass in nanograms.

- **Calculation Reporting Criteria**
  - Summary data table containing the following information. Some data may not be available based on procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
    - Data in ng/mL for the contract sampler extract (**CS_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
    - Analyte mass recovered (***Rec***) results in nanograms for each test replicate for each dosing solution.
    - Delivered mass results (***Del***) in nanograms for each dosing solutions, average Del and RSD.
    - Extraction efficiency (**EE**) calculated for each sample.
    - Which EE calibration curve was selected - Independent and Relative Recovery (IRR) or Power Law (PL).
    - The calibration curve slope and intercept.
    - Provide the selected calibration curve

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Delivered Mass: The delivered mass for the determination of the extraction efficiency test should produce analytical results with a RPD < 15%.

- Rationale: Due to the number of tools used and steps involved in preparing the dosing solutions, the most accurate method to calculate the delivered mass is to directly measure exactly what was delivered to the sample. This enables an accurate method to determine the extraction efficiency per test sample.

EE Model: The EE calibration model selected should provide a best fit to the data. Though some materials may provide a significant distribution of results, it is recommended that an average RPD value for a model is <15%. However, it is recognized that some materials may never meet this criteria. In all cases the average RPD value should be reported.

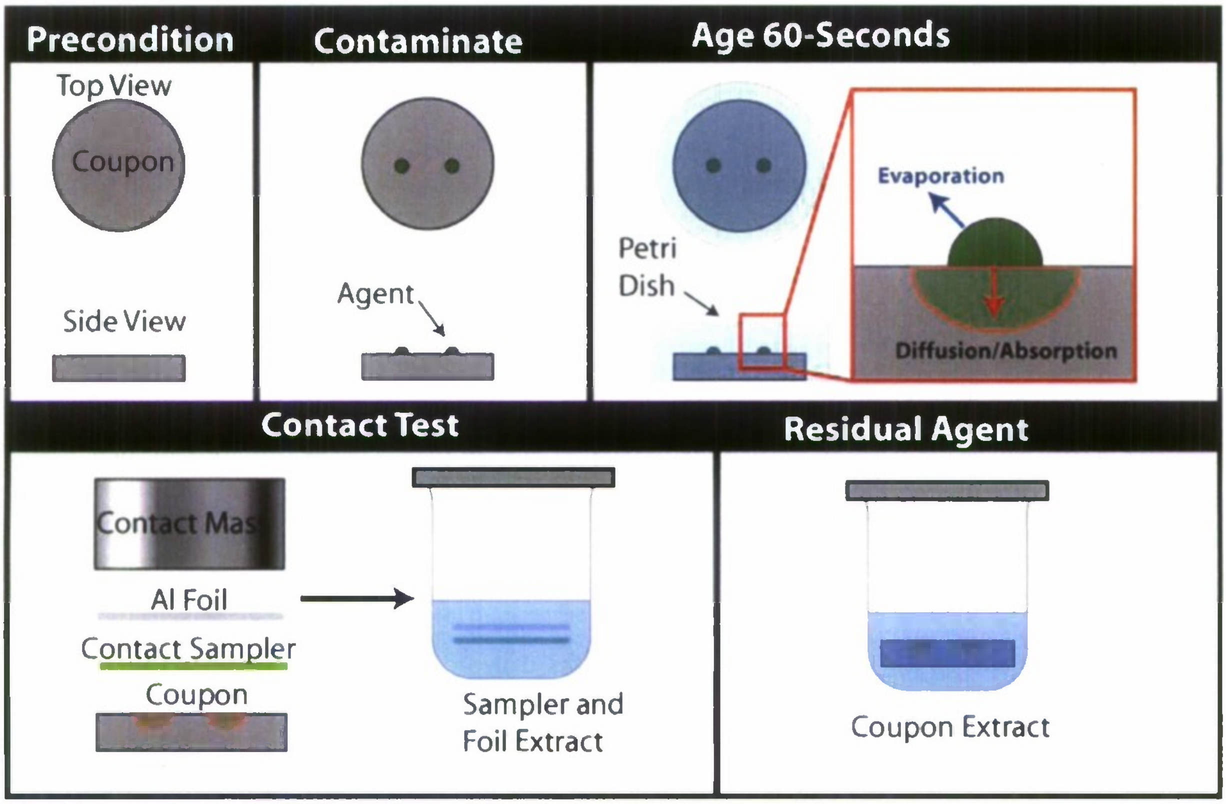
- Note: the EE calibration model assumes all loss is due to incomplete extraction. No correction is included that accounts for 'depth' in the material that may be harder to extract.

REVISION HISTORY

March 2008: original method.

PROCEDURE II – Contact Sampler Transfer Efficiency

The procedure specifies the core sampling handling, measurement, and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls/hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.



sketch Mantooth-Lalain 2007

Figure 6B-2. Contact Sampler Transfer Efficiency Test Sketch.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- Completion of test area setup, labeling (i.e., vials, trays, jars) and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing. Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).

- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- It is recommended that the contaminant equilibrates to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case, it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, rinse, and contact test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of five coupons per test condition and three dose-confirmation samples per contamination set.

2.0 Contaminate Coupons

2.1 Place coupons with area to be contaminated facing upwards on the temperature controlled surface set to 30 ± 5 °C (86 ± 9 °F)) is preferred. The value should be within ± 10 °C. If the value is greater than ± 10 °C, this must be clearly reported.

2.2 The contamination used to select the contact sampler utilizing a contamination density of 1-1.2 g/m^2 is applied using pipette (or equivalent tool) as two 1 µL drops placed in the 2 in. circular test area non-touching.

2.3 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

2.4 Fit pipettor with clean appropriate pipette tip

2.5 Load contaminant delivery tool in accordance with manufacturer's directions

2.6 Deliver to the surface the appropriate number of drops to achieve the contamination density. Repeat as needed for total number of coupons. Treatment time starts after the coupon is contaminated. Use of timing charts for multiple samples is recommended.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests) or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

2.7 If using pipettes or syringes to deliver contaminant, prepare the "dose-confirmation" sample. At least three replicate samples is recommended.

2.7.1 Delivering to a scintillation vial the appropriate number of drops to achieve the contamination density.

2.7.2 Add 20 mL of extraction solvent.

2.7.3 Cap vial

2.7.4 Thoroughly mix contents by inverting vial three times.

2.7.5 Using a clean, disposable pipette load the GC vial with aliquot of extractant solution.

2.8 Allow the agent to reside on the coupon for 60 seconds

2.9 Complete the required reporting for this section.

3.0 Contact Test

3.1 Place the contact sampler on the coupon surface.

3.2 Place a 2 in. diameter circular piece of aluminum foil on the contact sampler. The aluminum foil is to prevent contaminant breakthrough to the contact mass.

3.3 For uneven or rough surfaces, place a thin foam layer on the aluminum foil. Specifications?

3.4 Place a contact mass onto the foam / aluminum foil layer

3.5 Wait contact sampling period of 15 min

3.6 At the end of the sampling period remove the contact mass and foam (if used)

3.7 Place the contact sampler and aluminum into a scintillation vial (or equivalent glass container). The aluminum foil is extracted with the contact sampler to ensure any breakthrough mass is collected.

3.7.1 Add 20.0 mL of extraction solvent

3.7.2 Place teflon-lined lid on extraction scintillation vial.

3.7.3 Thoroughly mix contents by inverting vial three times

3.8 Extract the coupon

3.8.1 Place the coupon in an extraction jar. For most materials the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

3.8.2 Add 20.0 mL of extraction solvent ensuring coupon completely immersed.

3.8.3 Place PTFE/ Teflon-lined lid on extraction jar.

3.8.4 Swirl jar

3.9 Contact sampler/aluminum and coupon will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Method 6-B must match extraction time used in main test (e.g., Procedure 6-A, 6-D, 6-E).

3.10 At the end of the contact sampler extraction period, thoroughly mix the contents by inverting the vial three times. Open vial and, using a clean pipette tip, place a sample into a GC vial for analysis.

3.11 At the end of the coupon extraction period, swirl jar, open vial and using a clean pipette tip place a sample into an analytical vial for analysis

3.12 At the end of the coupon extraction period, Swirl jar, open vial and using a clean pipette tip place a sample is placed into a GC vial for analysis.

3.13 Complete the required reporting for this section.

4.0 Chromatographic Analysis for Agent

4.1 Samples are analyzed based on guidance in Procedure 6-H. This test generates three types of samples for analysis

- Dose confirmation
- Contact sampler extract
- Coupon extract

4.2 Sample dilution may be required for the sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

4.3 Obtain list of analytical results in ng/mL which already accounts for any additional dilutions beyond initial extraction.

4.4 Complete the required reporting for this section.

5.0 Perform Calculations

5.1 Obtain the analytical results for

- Dose confirmation
- Coupon extract

5.2 Perform calculations.

5.3 Complete the required reporting for this section.

CALCULATIONS

This procedure calculates the percent of mass that was delivered to a coupon and transferred to a contact sampler, as a variable called Transfer Efficiency (TE). This TE should not be used to correct data. The TE provides one way to compare different materials used as contact samplers. TE may be specific to coupon material-agent-contact sampler combinations.

1.0 Prepare Results Table

1.1 Obtain the chromatography data in ng/mL for the contact sampler extract (**CS_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis. Due to the dynamic range of the data included in this analysis several analytical methods may be used to analyze the samples. If there is a sample that reports a non-detection value and there is an analytical method with a lower detection limit, the sample should be re-run on the more sensitive method.

1.2 Convert the contact test result from mass in solution (**CS_E**) to mass (**CS_M**)

For each contact sampler extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{CS_M} \text{ (in ng)} = \mathbf{CS_E} \times \mathbf{EV} \quad (1)$$

1.3 Obtain the calibration curve developed from Procedure 6-B.

1.4 Calculate the extraction efficiency corrected contact test result (**CS_C**) in nanograms using the equation identified in Step 4.0 of Procedure 6-B.

1.5 Calculate 'Analyte Mass Delivered' ***Del***.

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\textbf{\textit{Del}} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

1.6 Calculate the average and standard deviation of the delivered mass for all replicates of each solution. (Acceptance criteria: the relative standard deviation (std/avg) must be < 15%)

1.7 Prepare results table for each dosing concentration listing the target mass on the coupon, delivered and recovered results.

1.8 Calculate the Transfer Efficiency (**TE**) for each sample which is calculated per Equation 3.

$$\mathbf{TE} = \mathbf{CS_M} / \textbf{\textit{Del}} \times \mathbf{100\%} \qquad (3)$$

1.9 If desired a TE calibration curve can be calculated (identical to the EE calibration curve) using Steps 2-4 of Procedure 6-B. Otherwise the TE of the contact sampler can be directly reported.

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test-specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.

EQUIPMENT

- **Contaminant Delivery Tool**
  - Tool identification including manufacturer, model number, and volume dispensing range.
  - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).

  - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
  - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Temperature Controlled Surface for Contact Test**: include tool identification including manufacturer and model number, and tool performance specifications if available.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Contact mass:** description including size, shape, material, and weight.
- **Contact sampler:** include the source, description, part number, lot, and any preparation or treatment (i.e., washing) performed.
- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (μL) per coupon.
  - Agent drop volume size(s) in microliters (μL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.

- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (μL) per vial, the agent drop volume size(s) in microliters (μL) per vial, the solvent identification, and the solvent volume.
- **Contact Test:** for each touch provide:
  - Temperature of controlled surface
  - Touch number
  - Contact sampling period in minutes
  - Time contact sampling period occurred post-decontamination. For example, a 15 minute contact sampling period started at 45 minutes and ending at 60 minutes post decontamination.
  - Extraction solvent
  - Extraction time
- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the contact test results in nanograms per coupon, "dose confirmation" sample mass in nanograms and residual agent coupon results in nanograms per coupon.
- **Calculation Reporting Criteria**
  - Summary data table containing the following information.
    - Data in nanograms per milliliter for the contract sampler extract (**CS_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
    - Contact test mass results (**CS_M**), not corrected for extraction efficiency in nanograms.
    - Delivered mass results (***Del)*** in nanograms.
    - Transfer Efficiency (**TE**) results in %

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the

conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the Amount of Contaminant Delivered in order to determine the difference. The Amount of Contaminant Delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Contaminated Surface Area (Contact): The contaminated surface area for a test set should have a small variance, although contaminant spreading on a material surface is a function of material-agent interactions. A large variance in the contaminated surface area could give false sense of test error; the cause of the variability should be investigated to determine if the data is acceptable. It is recommended to investigate if the variance in spreading is a property of the material-agent interactions or if it was a result of test procedures. If it was a result of test procedures the test should be rerun.

- Rationale: For sorptive materials the mass absorbed is proportional to the contaminated surface area (absorption is a flux-based process).
- Rational: For the contact test result, the agent mass sampled will be proportional to the contaminated surface area. The proportionality (e.g., square root area, linear area, area squared) is dependent on material properties and agent-material interactions.

- Note: The contaminated surface area immediately after contamination is likely to have little variation, however some material-agent combinations will result in spreading as a function of time, thus the pre-decon contaminated area may show a significant distribution. The pre-decon contaminated area should be used as the value to compare contaminated surface areas.
- Note: For comparison of data with different contaminated surface areas it is recommended to compare data using a mass per unit of contaminated surface area value rather than direct mass comparisons.

Contact Test Temperature: The contact test surface and contact masses temperature is 30 ± 5 °C (86 ± 9 °F).

- Rationale: This temperature is to represent the temperature of an extremity (e.g., hand) which is less than the core body temperature of 37 °C.
- Rationale: Mass transport coefficients typically double for every 10 °C. Temperature changes directly affects mass absorption into the contact sampler.
- Rationale: Contact masses may have significant thermal mass. Conducting tests without preheating masses may result in an inaccurate contact test temperature and variable mass absorption.

Contact Test Touch Time: The core contact test touch time is 15 minutes ± 45 seconds. If other touch durations are used the contact test touch time should be within ± 5% of the target total touch time.

- Rationale: The contact test result will vary with the contaminated surface area and touch length of time. For non-sorptive surfaces, the majority of mass adsorbed by the contact sampler is likely to occur within the first minute and is less affected by time. The contact touch time duration is directly proportional to contact test result for sorptive surfaces.

Contact Test Pressure: The core test contact test pressure is 0.7-1.0 psi (0.05-0.07 kg/cm^2), unless specified differently by test sponsor.

- Rationale: The pressure exerted on the contact sampler will determine the degree of contact between the contact sampler and the coupon. The contact sampler is usually a 'soft' material (i.e., low durometer) and will deform when pressure is applied. When more pressure is applied, the contact sampler will deform and increase the microscopic contact area due to 'filling in' the microscopic surface roughness of the sample and contact sampler. Increasing the pressure will increase the contact area which will increase mass absorption in the contact sampler. This has been documented in work by Schwope.
- Note: contact condition (wet vs. dry) has the same effect. If the coupon is wet, the water will 'fill in' the microscopic surface roughness and result in an increase in mass absorption in the contact sampler and may alter mass transport mechanisms.

Contact Sampler: The contact sampler is a simulant for human skin. The only guidance for material selection at this time is latex dental dam. The comparison of data using different contact sampler material may not produce similar results limiting direct comparison of test data.

- Rationale: The contact test is supposed to measure the mass of agent that would be transferred to skin. The mass of agent transferred to the contact sampler is a function of mass transport phenomenon that are material dependent (see EPA/600/8-91/011B 1992, *Dermal Exposure Assessment: Principles and Applications*). Materials with different mass transport properties will yield different mass absorption results. Comparison of contact results using different contact sampler materials is not advised.
- Note: the absorption rate of a contact sampler (skin or latex) is specific to the transport properties of the contaminated material, agent, and contact material. There is the possibility that skin and latex may have similar absorption rates on one material, but not on another.
- Note: The use of dental dam is recommended, though there is currently no published report characterizing the difference between this material and skin transport from various materials.

REVISION HISTORY

March 2008: original method.

Test Procedure 6-C: Rinsate Analysis for Agent Test Method

SUMMARY OF PROCEDURE

The rinsate analysis method is the measurement of the amount of agent physically removed from the coupon during the decontamination process.

This method is anticipated to be part of the FY08 release.

REVISION HISTORY

March 2008: this is a new method slated for development in the FY08 program.

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Test Procedure 6-D: Baseline Contact Test Method

SUMMARY OF PROCEDURE

The baseline contact test method is a complementary procedure to the Laboratory-Scale Decontaminant Performance Evaluation for Contact Test Method serving as either a positive- (contaminant, no decontaminant) or negative- (no contaminant, decontaminant) control. The most common use is a positive control test to measure the contact and residual agent when decontaminant is not used. It should not be assumed that the positive control test will result in measurable agent. A reduction in agent compared to the starting challenge may be observed in the test results as a result of agent loss during the decontamination process due to weathering / evaporation. The negative control test is used without contaminant to determine the impact the decontaminant has on the process. For example, aggressive decontaminants may extract impurities out of test materials that might interfere with analytical detection. The positive and negative control baseline tests are identified as Option 1 and Option 2, respectively. This test procedure is conducted using the selected parameters from test Procedure 6-A. This method can be used to evaluate decontaminant performance against liquid-phase contaminants such as chemical-warfare agents, chemical-warfare agent simulants, toxic-industrial-chemicals, and toxic-industrial-materials. The terms contaminant and agent are used interchangeably. This test is for the dry-skin case.

This procedure provides the following information:

- **The mass of agent in nanograms recovered from the contact sampler.**
- **The mass of agent in nanograms recovered from the coupon.**

The following prerequisite tests are required for this test procedure:

- Procedure 6-B, "Contact Sampler Extraction- and Sampling-Efficiency Test Method" is the method for determining the extraction efficiency of residual agent in or on the contact sampler using the solvent selected for testing.
- Procedure 6-F, "Panel (Coupon) Extraction Efficiency Test Method" is the method for determining the efficiency the selected solvent has for recovering agent from the coupon.
- Procedure 6-H, "Chromatographic Analysis Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

This procedure alone does not provide the complete assessment of the decontaminant's performance for reducing the agent contamination or reporting the hazard. The complete assessment of a decontaminant performance should also address:

- The amount of agent physically removed from the coupon during the decontamination process using either liquid decontaminants or post-decontamination rinsing step.
  - Procedure 6-C, "Rinsate Analysis for Agent Test Method" is the measurement of the amount of agent physically removed from the coupon during the decontamination process.
- The determination of percent neutralization and reduction in starting challenge is best addressed through the direct measurement of the amount of remaining agent post decontaminant.
  - Procedure 6-E, "Panel (Coupon) Extraction Method to Determine Remaining Agent" is the process for extracting, measuring, and reporting the residual agent in or on the coupon.
- Reporting the contact hazard value in mg/m^2.

   - Procedure 6-G, "Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy, or Reduction in Starting Challenge" is the process for converting the mass of agent recovered from the contact sampler to a reported hazard value.
- Reporting percent neutralization, percent efficacy, or reduction in starting challenge in g/m^2.
   - Procedure 6-G, "Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy or Reduction in Starting Challenge" is the process for converting the mass of agent recovered from the contact sampler to a reported hazard value.

Limitations and other test variations:

- This complete process provides the contact-test result for the first 60 min after decontamination. The hazard for 24 hours post decontamination cannot always be assumed the same as the 60 minute value.
   - **Sorptive / Porous materials**: Re-emergence of entrained agent from sorptive materials may pose a future hazard. The residual agent extraction test is recommended to identify any potential future hazard. Sorptive materials will typically have a significant residual agent post-decontamination requiring the proper documentation that a potential hazard may exist beyond the timepoint studied. If residual agent is present, then the contact-hazard at times beyond those tested must be reported as uncertain. As a result, the current guidance for many of these materials is replacement if contaminated.
   - **Nonsorptive materials**: Nonsoprtive materials typically yield low to no-detectable residual agent which may allow for time extrapolation of the 60 minute value out to longer time periods. A reported value that is an estimate or extrapolation outside the collected dataset must be clearly marked as such.
- **Contaminant Simulant:** Chemical compounds for chemical agents are often used during early screening or at non-chemical agent surety facilities. A chemical agent simulant is a chemical compound of lower toxicity than the chemical agent with at least one property similar to the chemical agent such as certain bonding, functional group, physical property, etc. Simulants should be selected based on the main property being tested for most accurate comparison. Since simulants do not contain all of the same physical and chemical properties of the live agent, simulant data alone is not sufficient to determine decontaminant performance. It is recommended that the simulant performance be confirmed with agent data.
- **Skin Simulant:** The ability to test every decontaminant–contaminant–material combination on real skin is not realistic. A skin simulant is used to estimate the contaminant transfer that may occur if the surface of interest was contacted with real skin. The selection of the contact sampler is not trivial, as thie ability to emulate skin requires careful consideration. The recommended material per reported toxicology information is latex dental dam, preferably unflavored, uncolored, and heavy gauge (0.01 in. thick). The use of materials with properties significantly different than skin may result in the collection of more or less agent. Comparison of data using different contact samplers should factor in the material uptake characteristics in the interpretation of the results.
- Certain variations fall outside the scope of the Laboratory-Scale Performance Evaluation test methods. This test method is only directly applicable to panels,

items or other test surfaces that can be sampled with the contact sampler and mass, and extracted in solvent. Complex coupons or articles requiring wiping or alternate swabbing procedures are outside the scope of this method.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA). In this case, the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample** - liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **bioavailable** – in toxicology, the degree to which a substance becomes available to the target tissue after administration of a defined exposure. In regard to the contact test, the contaminant mass transferred to the contact sampler that could be biologically available under appropriate conditions.
- **breadboard, brassboard, prototype** – technology in differing degrees of configuration still under development that is not in its final form. This can apply to test fixtures, formulations, and/or the decontamination system / applicator.
- **chemical agent** - a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contact hazard** - the amount of contaminant remaining on the surface that, based on toxicological human estimates, could pose a threat to unprotected personnel touching the contaminated surface.
- **contact mass** - a uniform mass used to apply pressure during the contact test. The masses are typically prepared from stainless steel. The masses should evenly exert 0.7-1.0 psi (0.05 to 0.07 kg/cm^2) pressure on the coupon surface. For the 2 in. diameter disk, this is equivalent to a 2 in. diameter cylindrical mass weighing 1 kg.
- **contact sampler** - material used in this contact test as a surrogate for human skin. The sampler sorbs the available surface contamination which is then extracted to determine the mass of agent potentially bioavailable or available for contact transfer.
- **contact sampler transfer efficiency** - the measurement of the contact sampler's ability to collect the contaminant from the test material (e.g., coupon). More specifically, the contact sampler's ability to sorb the analyte under the ideal case by using a nonsorptive material. Transfer efficiency may be different for various material-agent combinations.

- **contact transfer -** the capability for a contaminant present on a specific surface to be moved to another through touching the contaminated surface.
- **contaminant -** a chemical compound with harmful effects to humans that is to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemicals, and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant -** for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process -** the process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically for these procedures, the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing, and drying.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample –** sample providing the mass of the contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer's specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction –** the separation of a component from a mixture through selective solubility.
- **extraction efficiency -** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).

- **foam -** spongelike material used in the contact test to ensure contact mass pressure is evenly applied to the test surface.
- **hazard -** A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property, or mission degradation. (reference FM 3-11.9)
- **limit of detection –** LOD see *detection limit.*
- **limit of quantitation –** LOQ see *quantitation limit.*
- **moderate condition** - test condition in middle of the testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization -** the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption, though there may be a minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **operational decontamination** – decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material, and/or working areas, in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **percent efficacy (and calculation) -** the measurement of the amount of contaminant removed from the material of interest as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **percent neutralization (and calculation)**: the measurement of the amount of contaminant reacted/neutralized as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **quantitation limit** –the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **reduction in starting challenge (and calculation)** – the measurement of the mass of contaminant that has been removed from the material of interest. This calculation is most often employed for the evaluation of physical removal, sorbent, or pre-clean techniques. The value can be reported as calculated, approximated, or inferred.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **remaining agent -** the amount of contaminant present in / on the material of interest after the decontamination process has been conducted. This value is different from the residual agent in that no mass has been removed from the coupon by contact or vapor testing. This value cannot be used to calculate a contact- or vapor-hazard.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).

- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate** - the collected rinse from the decontamination process. Sample may include residual decontaminant, agent, or agent byproducts in water.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface, it is better described as a thin film.
- **skin simulant** – material used in the contact test to estimate the contaminant transfer that may occur if the surface of interest was contacted (e.g., touched) by real skin. See test limitations regarding use for contact testing.
- **sorptive or porous materials** - a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition** - for a specific agent – material- decon set the combined contamination, aging, decontaminant process, environmental, and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **touch** - a contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). For the coupon test, the contact area is nominally the coupon area. The pressure is 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure which is equivalent to a 1 kg contact mass that is cylindrical with a 2 in. diameter. The contact time is typically 15 min.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.9, Potential Military Chemical/Biological Agents and Compounds, 10 January 2005.
- Headquarters, Department of the Army (DA), Washington, DC, Army Manual (AR) 70-38, Research, Development, Test and Evaluation of Materiel for Extreme Climatic Conditions, 15 September 1979.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.

- Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
- Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
- Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.

- **Decontaminants:** The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid- or vapor-phase and may contain a reactive functionality for neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Extraction solvents:** The test requires the extraction of sorbed agent from test materials such as the contact sampler and/or coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride, and solvent blends.

Water: Decon processes typically involve a post-rinse step, and some decontaminants are made using water. Laboratory testing will use distilled or deionized water unless otherwise instructed by the test sponsor.

EQUIPMENT

The equipment required for this method includes tools for delivering the contaminant, the decontaminant and rinse water, maintaining environmental control and preparing analytical samples. Several equipment options exist, ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision, and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (µL) which is equivalent to a 1 and 10 g/m^2 starting challenge,

respectively. Example: the core coupon test specifies using a total contamination volume of 2 µL delivered as two 1 µL drops for a 1 g/m^2 starting challenge.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. They are also best suited for pipetting volatile liquids. The smallest delivery volume, based on a survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
- Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. The smallest delivery volume based on a survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
- Computerized Dispensing System: Automated tool with the ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.

- **Decontaminant Delivery Tool:** the tool used to deliver a specific volume of decontaminant to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The core coupon test specifies using a decontaminant volume of 0.100 to 1.00 mL. The specific decontaminant under evaluation may use other delivery volumes.
  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of decontaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
  - Spray Bottle: Some applications will mimic a spray application using a spray bottle. The tool should be evaluated to determine the number of pumping actions required to achieve the target decontaminant application. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- Developmental Breadboard, Brassboard, or Protoype Technology: These are technologies under development that are not in their final configuration. The decontaminant generation and delivery may not be known. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- Vendor Provided Technology: This is equipment provided from vendor that may be breadboard, brassboard, prototype, or commercial in configuration. The technology is operated per vendor guidance. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Water Rinse Delivery Tool:** Tool for the delivery of specific volumes of water to the coupon surface to remove decontaminant from the surface. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. It is recommended that the tool used has the ability to control the flow rate in order to reduce operator-to-operator variations. The typical delivery volume for a 2 in. diameter circular contamination area range is 60 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. An example is the Dispensette and Brinkman brands. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
  - Pump: Other precision liquid dispensing systems. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test. Tools obtained or developed by the testing laboratory which has no performance specification standards or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be

used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.

- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
    - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.
- **Temperature Controlled Surface for Contact Test:** The lab-scale testing uses a temperature controlled surface to mimic body temperature regulated at 30 ± 5 °C (86 ± 9 °F). The value should be within ± 10°C. If the value is greater than ± 10°C, it must be clearly reported.
    - Slidewarmer: temperature controllable surface typically used in histological testing. Tools obtained or developed by the testing laboratory which has no performance specification standards or vendor provided performance information must be tested to determine their accuracy and precision.
- **Environmental Chamber:** Temperature and relative humidity controlled chamber for the preconditioning and aging of coupons. The fixture should be able to maintain test specific environmental conditions (e.g., temperature and relative humidity) even when adding or removing samples. The system must have temperature and relative humidity data logger capability, and be able to store and download temperature and humidity data and traces to a computer for further analysis. The system must be able to maintain temperature and relative humidity. The system operation and range should be known.
- **Contaminated Area Measurement:** Fixed-site photographic setup to visually capture the agent contamination surface area coverage after dosing, aging, and any other critical steps in the decontamination process. Photograph resolution of 9–25 pixels per droplet measured is recommended for surface area calculations.
    - Digital Camera on Fixed Stand
    - Imaging Station
- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Method 6-H. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas

and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may also be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space, protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Contact mass(es):** A laboratory scale contact test utilizes a mass to deliver 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure during the contact touch. For the 2 in. disk, the mass is a stainless steel, 2 in. in diameter cylinder weighing 1 kg, placed onto the sample surface for the duration of the contact time.
- **Contact sampler(s):** Adsorptive material used to collect available contamination from surface of interest. The use of latex dental dam, preferably unflavored, uncolored, and heavy gauge is suggested. Testing will typically use 0.01 in. thick material.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the contact sampler and/or coupon. A glass container such as a vial or jar of sufficient size to hold both the contact sampler and/or coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample. The use of plastic containers is not recommended for chemical agent testing.
- **Foam**
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** typically used during the aging step to cover the coupon surface in order to minimize evaporative loss. They can also be used as a sample holder.
- **Rinsate collection container:** If rinse water analysis is required, the rinse should be collected in a glass container of sufficient volume for the rinse water and extraction solvent, preferably a wide mouth jar. It is recommended to limit use of funnels or other tools that may uptake agent during collection. The use of plastic containers is not recommended for chemical agent testing. The container cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers, or tongs.

- **Standard laboratory record keeping items:** record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **Timing device(s):** The test method requires accurate timing of key steps. Digital timers reporting in minutes and seconds are preferred.
- **Transfer pipettes**
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balances, stir plates, stir bars, vortexer, and pH meters.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health, and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices, including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement, and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.

This test has Options 1 and 2 for the positive- (contaminant, no decontaminant) or negative- (no contaminant, decontaminant) control, respectively. This test aligns with test Method 6-A requiring the use of the identical test process used. Test Procedure 6-A has Options A, B and C that are step variations based on potential variables that could be explored. The core test evaluation is designated by Option A. This option is based on a liquid decontaminant tested at moderate environmental conditions using equipment with known accuracy. This option should be used unless otherwise instructed by a test sponsor. Option B is similar to Option A but allows for different parameters, such as temperature. Option C is designed for the evaluation of new technologies or the use of conditions outside of the core test. The use of lettering does not indicate a test grade. The letter serves as a quick reference to the selections made during testing and the considerations required for comparing different groups of data. Options A and B parameter choices are preferred in cases where lab-data must be compared to requirements; however, Option C parameters may need to be used, especially for the evaluation of new technologies.

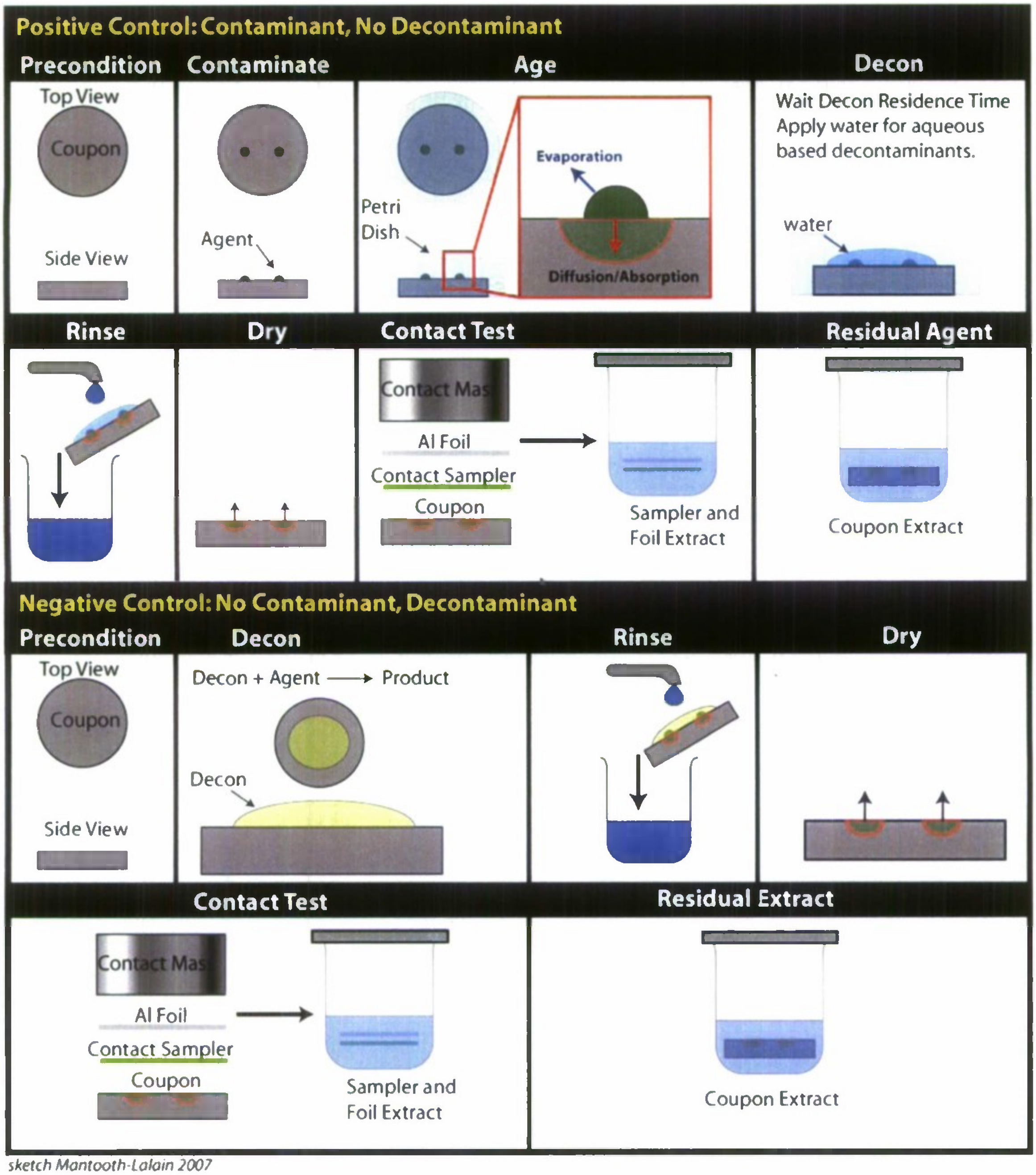


Figure 6D-1. Positive and Negative Control Test Sketch.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to beginning the test. Preparation tasks for this method may include:

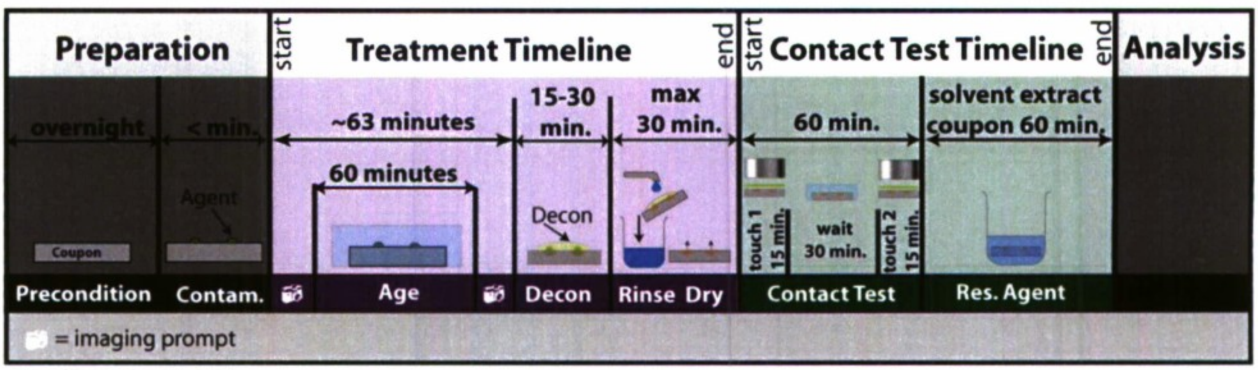
- **Identify the calculation desired: contact-hazard, percent neutralization, percent efficacy, or reduction in starting challenge. Review calculation**

Method 6-G and select the appropriate test methods and options within a test method to ensure the necessary data is collected.

- Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars), and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Decontaminant preparation.
- Obtaining the Procedure 6-A process to be used.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- It is recommended that the contaminant equilibrates to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case, it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, rinse and contact test times is strongly encouraged, as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of five coupons per test condition and three dose-confirmation samples per contamination set.



sketch Mantooth-Lalain 2007

Figure 6D-2. Contact Test Timeline Representation for Procedure 6-A Option A.

2.0 Precondition Coupons

2.1 Set the environmental chamber to the specified test condition

METHOD 6–A OPTIONS:

OPTION A (core test): **moderate condition** test using the environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported.

OPTION B (core test, variable condition): variable condition test with the environmental chamber using test sponsor / director temperature and relative humidity set-point. The most common test cases are high and low temperature and relative humidity.

OPTION C (outside core test): This test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupon conditioning is to occur using the same method including temperature, relative humidity, location, and time as that used in Procedure 6-A .

OPTION 2 - Negative Control (no contaminant, decontaminant): the coupon conditioning is to occur using the same method including temperature, relative humidity, location, and time as that used in Procedure 6-A .

2.2 Allow the environmental chamber to equilibrate at the set-point temperature and relative humidity. The time to reach set-point equilibration may vary. It is recommended that the temperature and humidity are maintained at the set-point for at least 30 min. prior to the start of testing.

2.3 The coupons are placed horizontally on coupon trays with the test surface to be contaminated / decontaminated facing upwards.

2.4 Once the chamber has equilibrated at the set-point temperature and relative humidity, place the trays into the environmental chamber for at least 60 min. The recommended practice if possible is to precondition the test materials overnight.

- Note: Some materials may require special preconditioning treatments. For example, cellulose based materials and concrete contain significant moisture. These types of materials do not typically achieve moisture equilibrium in less than 24 to 48 hours. Longer precondition times may be required for certain materials. An example procedure for wood is ASTM D4442.

2.5 Samples should not be removed until ready to execute Step 3, Contaminate Coupons.

2.6 Complete the required reporting for this section.

3.0 Contaminate Coupons

3.1 Identify the contamination density, including the number of drops, drop volume, and deposition pattern.

METHOD 6–A OPTIONS:

OPTION A (core test): The contamination density is 1-1.2 g/m^2 applied using a pipette / syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area, non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): The variable contamination density is typically between 1 to 10 g/m^2 applied using pipette / syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

OPTION C (outside core test): The application of agent is done using brushes, roller,s or spras applicators such that the amount of agent applied to the specific surface is not tightly quantifiable. Note: calculation of percent neutralization might not be feasible using this option.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupon contamination is to occur using the identical process used for the Procedure 6-A testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied.

3.2 Set tool to appropriate drop volume

- Note: The pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with clean, appropriate pipette tip

3.4 Load the contaminant delivery tool in accordance with manufacture's directions

3.5 Deliver to the surface the appropriate number of drops to achieve the contamination density. Reload the tool and repeat as needed for the total number of coupons. Treatment time starts after the coupon is contaminated. The use of timing charts is recommended for multiple samples.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests), or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.6 If using pipettes or syringes to deliver the contaminant, prepare the "dose confirmation" sample. At least three replicate samples are recommended.

3.6.1 Deliver to a scintillation vial the appropriate number of drops to achieve the contamination density.

3.6.2 Add 20 mL of extraction solvent.

3.6.3 Cap vial

3.6.4 Thoroughly mix contents by inverting the vial three times.

3.7 Observe the post-contamination drop interaction with the surface and surface coverage.

METHOD 6–A OPTIONS:

OPTION A (core test): using a digital camera or imaging station, photograph each coupon surface.

OPTION B (core test variable condition): Some materials may not allow for rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three independent coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): if digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered should be documented both in words and with a hand drawing.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical process used for the Procedure 6-A testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied, skip to step 5.

3.8 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

3.9 Complete the required reporting for this section.

4.0 Coupon Aging

4.1 Coupons are aged.

METHOD 6–A OPTIONS:

OPTION A (core test): Coupons are aged in environmental chamber for 60 min at a moderate condition test with an environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. The environmental chamber should have logging capability for real-time temperature and humidity recording.

OPTION B (core test, variable condition): Coupons are aged in an environmental chamber under one or more of the following cases. The environmental chamber should have logging capability for real-time temperature and humidity recording.

- Variable temperature and relative humidity: aging conducted at test sponsor / director designated temperature and relative humidity.
- Variable aging time: Shorter aging time for immediate or operational decon applications, or an aging period longer than the Option A basic thorough test. The aging may be at the moderate condition and/or variable temperature and relative humidity.

OPTION C (outside core test): This test is conducted at room conditions without the use of an environmental chamber. Note that the room condition is the temperature at the test location on a given test day. This could be warm, moderate, or cold.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupons are aged using the identical procedure as the Procedure 6-A testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): skip to step 5.

4.2 Observe the post-aging drop interaction with the surface and surface coverage. (If no aging period is used, this step can be skipped).

METHOD 6–A OPTIONS:

OPTION A (core test): Using a digital camera or imaging station, photograph each coupon surface. There is a chance that for some materials the post aging image may not be visible without use of a color indicator or dye.

OPTION B (core test variable condition): Some materials may not allow for rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered should be documented both in words and with a hand drawing.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical process used for the Procedure 6-A testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied.

4.3 Complete the required reporting for this section.

4.4 Coupons are moved to decontamination test area at end of aging period.

5.0 Pre-rinse the Coupons

5.1 Coupons are rinsed.

METHOD 6–A OPTIONS:

OPTION A (core test): pre-rinse is not used for the core test.

OPTION B (core test variable condition): Pre-rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in a glass jar for processing and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION C (outside core test): The use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water falls outside the core test as the rinse evaluation method needs to be completed to determine the impact of surfactants on accurate agent measurement.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-A should be used here.

5.2 Complete the required reporting for this section.

6.0 Decontaminate the Coupons

6.1 Apply decontaminant

METHOD 6–A OPTIONS:

OPTION A (core test): For the core test there are a few sub-options based on the test objective. The decontaminants are liquid-phase and applied using a pipette. Dispensettes or pumps may fall under Option A if the decontaminant delivery volume to the contaminated region can be accurately measured. Unless otherwise specified, the decontaminant applied is typically at room conditions. The amount of decontaminant applied is based on the following guidance.

- Option A-1: For early research tests, it is recommended that 1.00 mL of decontaminant is evenly dispensed over the contaminated coupon surface in a single application. Care should be taken to ensure that the decontaminant is delivered uniformly over the test area. This recommended decontaminant

volume is for starting challenges in the 1 to 10 g/m^2 range to ensure that decontaminant covers the contaminated surface area. Some agent-material interactions could result in significant contaminated surface coverage that smaller decontaminant volumes may not be able to adequately cover the entire contaminated surface yielding data scatter due to decontaminant delivery.

- Option A-2: FM 3-11.5 recommends a decontaminant to contaminant ratio of 50:1. This corresponds to 0.100 mL to 1.000 mL for a 1 to 10 g/m^2 starting challenge, respectively.

OPTION B (core test variable condition): Some liquid-phase decontaminants may require applying more or less decontaminant. For vapor-phase decontaminants, apply the appropriate fumigant concentration.

OPTION C (outside core test): Tthe use of solid decontaminants, sorbent wipes, brushing, or mechanical scrubbing methods are outside the scope. These materials have the potential to retain or physically relocate agent. The use of these methods requires adjustment to calculating percent neutralization. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes falls here. Decontaminant is applied as best as possible in accordance with technology operating procedures.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): decontaminant is not applied.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-A should be used here.

6.2 Cover coupons with a Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

6.3 Wait the appropriate decontaminant residence time at the specified environmental condition

METHOD 6–A OPTIONS:

OPTION A (core test): The standard decontaminant residence time is from 15 to 30 min for liquid-phase decontaminants in an environmental chamber at ambient conditions with an environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. The environmental chamber should have charting capability for real-time temperature and humidity logging.

OPTION B (core test variable condition): liquid-phase decontaminants outside the 15 to 30 minute range or at variable temperature or humidity that are placed in environmental chamber for a specified residence period.

OPTION C (outside core test): liquid phase decontaminants evaluated at room condition. Sorbents and wipes may have other residence times on the surface. Vapor-phase decontaminants may dictate environmental conditions as part of the process. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes using residence times outside the core 15 to 30 min or environmental conditions outside the specified test conditions fall here.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): The baseline study uses the identical procedure from Procedure 6-A. The identical decontaminant residence time, temperature, and relative humidity should be used. If the decontaminant process utilizes air movement (i.e., vaporous decontaminants), the identical process parameters and decontaminant residence time should be used.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-A should be used here.

6.4 Complete the required reporting for this section.

7.0 Post-Rinse and Dry

7.1 Coupons are rinsed.

METHOD 6–A OPTIONS:

OPTION A (core test): Rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for processing and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION B (core test variable condition): Rinse is not collected or analyzed.

OPTION C (outside core test): The use of pressure washers falls outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time, hot soapy water falls outside the core test as the rinse evaluation method needs to be completed to determine the impact of surfactant on accurate agent measurement. Some decontaminants do not require a post rinse. The impact of residual decon on the contact test analytical measurements must be evaluated.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-A should be used here.

7.2 Coupon drying

METHOD 6–A OPTIONS:

OPTION A (core test): Passive drying is recommended at room conditions, preferably in a chemical fume hood (or equivalent) with approximately 100 linear feet per minute (lfm) airflow. The coupons are recommended to be placed at an angle to increase air flow over the surface. Coupons should not be dried for more than 30 min. Residual water on the surface should be noted. For most applications, wicking the last bead of rinse water should have little impact on the results.

OPTION B (core test variable condition): Controlled air drying which is an active blowing with established air temperature, flow rate, etc.

OPTION C (outside core test): Blotting, wiping, or other direct surface contact methods that may also remove agent as part of the process. These methods can impact contact measurement. No drying would also fall here, as residual water affects the contact measurement if trying to conduct the dry-skin equivalent contact test.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-A should be used here.

7.3 Complete the required reporting for this section.

7.4 The coupon treatment process is considered complete once the surface of interest has dried or the 30 minute drying time has elapsed. The contact test time is initiated as shown in Figure 6D-3.

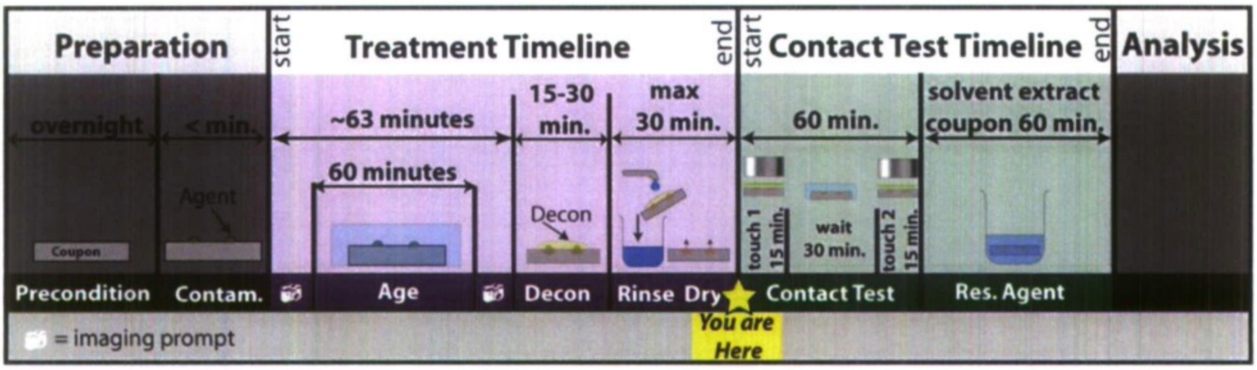


Figure 6D-3. Contact Test Timeline Representation for Option A.

Note: Reproduction of this sketch must carry sketch credit to Mantooth-Lalain.

8.0 Contact Test

8.1 A contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). The contact test is the process of applying the contact sampler to the coupon surface for a specified duration of time. The number of contact sampling periods is referred to as "touches."

8.2 Conduct first touch

8.2.1 Place the coupon on the temperature controlled surface set to 30 ± 5 °C (86 ± 9 °F) is preferred. The value should be within ± 10 °C. If the value is greater than ± 10°C, this must be clearly reported.

8.2.2 Place the contact sampler on the coupon surface.

8.2.3 Place a 2 in. diameter circular piece of aluminum foil on the contact sampler. The aluminum foil is to prevent contaminant breakthrough to the contact mass.

8.2.4 For uneven or rough surfaces, place a thin foam layer on the aluminum foil.

8.2.5 Place a contact mass onto the foam / aluminum foil layer.

8.2.6 Wait the contact time.

OPTION A (core test): the first touch is 15 min in length, occurring immediately after decontamination (dry step 7.4) is completed.

OPTION B (core test variable condition): sampling period is 15 min in length occurring at a different time point post end of decontamination.

OPTION C (outside core test): a sampling period other than 15 min.

8.2.7 At the end of the sampling period, the contact mass and foam (if used) are removed.

8.2.8 Place the contact sampler and aluminum into a scintillation vial (or equivalent glass container). The aluminum foil is extracted with the contact sampler to ensure any breakthrough mass is collected.

8.2.9 Cover coupon with Petri dish to minimize cross contamination and evaporative loss.

8.2.10 Add 20.0 mL of extraction solvent.

8.2.11 Place a PTFE/ Teflon-lined lid on extraction scintillation vial.

8.2.12 Thoroughly mix contents by inverting the vial three times

8.2.13 The contact sampler / aluminum will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Method 6-B must use the same extraction time.

8.2.14 At the end of the extraction period, thoroughly mix the contents by inverting vial three times

8.2.15 Using a clean pipette, place a sample into an analytical vial for analysis.

8.3 For the core test, wait 30 min. If no other touches are to be performed, skip to step 8.5.

8.4 Conduct second touch.

OPTION A (core test): The first touch typically has a large data scatter. The second touch is recommended for completeness. The process is the same as Step 8.2, if conducted.

OPTION B (core test variable condition): The second touch is skipped, and proceeds directly to residual agent measurement.

OPTION C (outside core test): additional sampling periods beyond the first touch, as directed by the test sponsor / director.

8.5 After the last touch is complete, the coupon can be extracted for residual agent.

8.5.1 Place the coupon in an extraction jar. For most materials, the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

8.5.2 Add 20.0 mL of the extraction solvent, ensuring the coupon is completely immersed.

8.5.3 Place a PTFE/ Teflon-lined lid on the extraction jar.

8.5.4 Swirl jar.

8.5.5 The coupon will remain in the extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Method 6-B must use the same extraction time.

8.5.6 At the end of the coupon extraction period, swirl the jar, open the vial, and, using a clean pipette tip, place a sample into an analytical vial for analysis.

8.6 Complete the required reporting for this section.

8.7 The contact test is complete.

9.0 Chromatographic Analysis for Agent

9.1 Samples are analyzed based on guidance in Procedure 6-H. This test generates three types of samples for analysis

- Dose confirmation
- Contact sampler extract for contact test
- Coupon extract for residual agent

9.2 Sample dilution may be required for the sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

9.3 Obtain a list of analytical results in ng/mL which already for accounts any additional dilutions.

9.4 Complete the required reporting for this section.

10.0 Perform Calculations

10.1 Obtain the analytical results for

- Dose confirmation
- Contact sampler extract for contact test
- Coupon extract for residual agent

10.2 Perform all calculations.

10.3 Complete the required reporting for this section.

CALCULATIONS

1.0 Convert Results from ng/mL to ng

1.1 Obtain the chromatography data in ng/mL for the contact sampler extract ($\mathbf{CS_E}$), the residual agent extract ($\mathbf{RE_E}$), and the dose-confirmation samples ($\mathbf{DC_E}$) that have been corrected for any dilutions performed between sample collection and analysis.

1.2 Convert the contact test result from mass in solution ($\mathbf{CS_E}$) to mass ($\mathbf{CS_M}$).

For each contact sampler extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{CS_M} \text{ (in ng)} = \mathbf{CS_E} \times \mathbf{EV} \qquad (1)$$

1.3 Convert the residual agent test result from mass in solution ($\mathbf{RE_E}$) to mass ($\mathbf{RE_M}$).

For each residual agent extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{RE_M} \text{ (in ng)} = \mathbf{RE_E} \times \mathbf{EV} \qquad (2)$$

1.4 Calculate 'Analyte Mass Delivered' ***Del*** from dose confirmation sample

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL. Average results for replicates reporting the relative standard deviation.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (3)$$

2.0 Calculate the Contact Test Results Corrected for Extraction Efficiency

2.1 Obtain the calibration curve developed from Procedure 6-B.

2.2 Calculate the extraction efficiency corrected contact test result ($\mathbf{CS_C}$) in nanograms using the equation identified in step 4.0 of procedure 6-B.

3.0 Calculate the Residual Agent Results Corrected for Extraction Efficiency

3.1 Obtain the calibration curve developed from Procedure 6-F.

3.2 Calculate the extraction efficiency corrected contact test result ($\mathbf{CS_C}$) in nanograms using the equation identified in step 4.0 of procedure 6-F.

4.0 Complete the Required Reporting for this Section.

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Decontaminants:** Provide for each decontaminant used the decontaminant name / description, source, date of preparation, purchase or expiration date (as applicable). Include a description of the preparation process for materials requiring pre-use preparation such as dilution or mixing.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.
- **Water:** Provide a description of the water used and source for each use of water. For example, laboratory distilled water may have been used to mix the decontaminant and certified ocean seawater might have been used for the rinse. The water reporting would include the description for both the decontaminant prepared and rinse waters used. Include characterization data / specification sheet details for any certified or specialty water used.

EQUIPMENT

- **Contaminant Delivery Tool**
    - Tool identification including manufacturer, model number, and volume dispensing range.
    - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
    - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
    - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Decontaminant Delivery Tool**
    - *See contaminant delivery tool listing for pipettes and syringes.*
    - For breadboard, brassboard, and prototype equipment, provide a description of the decontamination system including configuration and identification number / name.
    - For vendor provided equipment, provide the vendor name, item description, and model number.
- **Water Rinse Delivery Tool:** *see contaminant delivery tool listing.*
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools**: *see contaminant delivery tool listing.*
- **Temperature Controlled Surface for Contact Test**: include tool identification including manufacturer and model number, and tool performance specifications if available.
- **Environmental Chamber:** Provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems. If a data logger is used, then include the data logging frequency.
- **Contaminated Area Measurement (if performed)**: include tool identification including manufacturer and model number, camera resolution, description of area measurement calculation and associated error with calculation if known.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Contact mass:** description including size, shape, material, and weight.
- **Contact sampler:** include the source, description, part number, lot, and any preparation or treatment (i.e., washing) performed.

- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Precondition Coupons**
  - Option used (A, B or C)
    - For Option C: a description of how the conditioning was performed.
  - Precondition length of time with units of hours and minutes.
  - Temperature average with standard deviation, high, and low for conditioning period.
  - Relative humidity average with standard deviation, high, and low for conditioning period.
  - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (μL) per coupon.
  - Agent drop volume size(s) in microliters (μL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (μL) per vial, the agent drop volume size(s) in microliters (μL) per vial, the solvent identification, and the solvent volume.
- **Post-Contamination Surface Contamination Observation**
  - Option used (A, B or C)
  - Written description of applied drops as they appear for each coupon (e.g., sessile, spread).
  - For Option B: how contrasting was achieved.
  - For Option A/B: provide a representative photograph
  - For Option A/B: provide the calculated contaminated surface area
  - For Option C: provide a hand drawing of the representative contaminated area, estimated contaminated surface area, and the method for estimating contaminated surface area.

- **Aging**
    - Option used (A, B or C)
        - For Option C: a description of how the aging was performed.
    - Coupon cover description including source, part number, size, and volume.
    - Aging length of time in units of minutes.
    - Temperature average with standard deviation, high, and low for aging period.
    - Relative humidity average with standard deviation, high, and low for aging period.
    - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Post-Aging Surface Contamination Observation:** *see requirements for Post-Contamination Surface Contamination Observation.*
- **Pre-Rinse**
    - Option used (A, B or C)
        - For Option C: a description of how rinsing was performed.
    - Rinse material identification (i.e., distilled water, hot soapy tap water, etc.).
    - Rinse material temperature
    - Test location temperature and relative humidity during rinsing.
    - Total volume applied
    - Description of the force and rate rinse applied
- **Decontamination**
    - Option used (A, B or C)
        - For Option C: a description of the decontamination process.
    - Description of the decontaminant application process.
    - Decontaminant temperature.
    - If decontaminant is applied "cold" or "warm" provide a description of how decontaminant was chilled or warmed.
    - Record amount of decontaminant applied
        - For liquids, volume delivered
        - For solids, mass delivered
        - For vapors, injection rate, flow rate, fumigant concentration, temperature, and relative humidity
        - Or other specifications per manufacturer's delivery instructions.
    - Coupon cover description including source, part number, size, and volume.
    - Decon residence time on coupon surface in minutes
- **Post-Rinse:** *see requirements for Pre-Rinse.*
- **Drying**
    - Option used (A, B or C)
        - For Options A, B and C: a description of how drying was performed.
        - For Option C: if no drying was used, provide a detailed description of how wet the surface was (representative photograph recommended).
    - Drying time in minutes
    - Description of drying location
        - If hood, specify air velocity
        - If flow chamber, specify flow rate and air temperature.
    - Temperature
    - Relative humidity
    - Description of any residual water on surface at the end of the drying period.
    - Detailed description of drying process used.
- **Contact Test:** for each touch provide:
    - Temperature of controlled surface
    - Touch number
    - Contact sampling period in minutes

   - Time contact sampling period occurred post-decontamination. For example, a 15 minute contact sampling period started at 45 minutes and ending at 60 minutes post decontamination.
   - Extraction solvent
   - Extraction time

- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the contact test results in nanograms per coupon, "dose confirmation" sample mass in nanograms and residual agent coupon results in nanograms per coupon.
- **Calculation Reporting Criteria**
   - Summary data table containing the following information. Some data may not be available based on procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
      - Data in ng/mL for the contract sampler extract ($\mathbf{CS_E}$), the residual agent extract ($\mathbf{RE_E}$) and the dose-confirmation samples ($\mathbf{DC_E}$) that has been corrected for any dilutions performed between sample collection and analysis.
      - Contact test mass results ($\mathbf{CS_M}$), not corrected for extraction efficiency in ng.
      - Residual agent mass results ($\mathbf{RE_M}$), not corrected for extraction efficiency in ng.
      - Delivered mass results (***Del***) in ng.
      - Extraction efficiency corrected contact test mass results ($\mathbf{CS_C}$) in ng.
      - Extraction efficiency corrected residual agent mass results ($\mathbf{RE_C}$) in ng.
      - Test set (combination of test replicates) averages and standard deviations for data sets specific to reporting results for test objective(s).
   - Summary of the contact sampler extraction efficiency determination (Procedure 6-B) for each contaminant -extraction solvent pair if Procedure 6-B was not directly executed and reported for this test report.
      - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
   - Summary of the coupon extraction efficiency determination (Procedure 6-F) for each agent – material - extraction solvent combination if Procedure 6-F was not directly executed and reported for this test report.
      - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
   - Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test

results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the Amount of Contaminant Delivered in order to determine the difference. The Amount of Contaminant Delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Aging Temperature and Relative Humidity: Core test moderate condition is 21 ± 3 °C, preferred, ± 5 °C maximum. Aging temperature in general is target temperature ± 5 °C. No criterion for RH is specified, however, a test sponsor may specify depending on test objective.

- Rationale: Changes in temperature directly affect the amount of contaminant absorbed into a material. Any deviation in temperature increases the amount of error in the end test result. Therefore, deviations in temperature must be minimized. For example, mass transport coefficients typically double for every 10 °C increase in temperature.
- Rationale: Relative humidity is expected to have a minor influence on test results compared to other system variables.

Aging Time: Core test aging time is 60 ± 3 min. For other aging times, the acceptance criterion is target time ± 5%.

- Rationale: The more or less time a contaminated coupon is aged, the more or less contaminant is absorbed into the coupon. For example, mass adsorbed for sorptive non-porous materials (based on Fick's first law) is proportional to square root of the aging time. A 5% time deviation could result in a 2.5% variation in mass absorbed into the coupon.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Amount of Decontaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered. In the event these criteria were not met, a repeatability study could be performed to determine the precision of the tool.

Decontaminant Residence Time: The total decontaminant residence time should be within ± 5% target time.

- Rationale: The measurement of the effect the decontaminant has for contaminant reduction is the main objective of the test. The decontaminant–contaminant interaction time will be proportional to the amount of agent removed and or neutralized, likely in a nonlinear manner.

Contaminated Surface Area (Contact): The contaminated surface area for a test set should have a small variance, although contaminant spreading on a material surface is a function of material-agent interactions. A large variance in the contaminated surface area could give false sense of test error; the cause of the variability should be investigated to determine if the data is acceptable. It is recommended to investigate if the variance in spreading is a property of the material-agent interactions or if it was a result of test procedures. If it was a result of test procedures the test should be rerun.

- Rationale: For sorptive materials the mass absorbed is proportional to the contaminated surface area (absorption is a flux-based process).
- Rational: For the contact test result, the agent mass sampled will be proportional to the contaminated surface area. The proportionality (e.g., square root area, linear area, area squared) is dependent on material properties and agent-material interactions.
- Note: The contaminated surface area immediately after contamination is likely to have little variation, however some material-agent combinations will result in spreading as a function of time, thus the pre-decon contaminated area may show a significant distribution. The pre-decon contaminated area should be used as the value to compare contaminated surface areas.
- Note: For comparison of data with different contaminated surface areas it is recommended to compare data using a mass per unit of contaminated surface area value rather than direct mass comparisons.

Contact Test Temperature: The contact test surface and contact masses temperature is 30 ± 5 °C (86 ± 9 °F).

- Rationale: This temperature is to represent the temperature of an extremity (e.g., hand) which is less than the core body temperature of 37 °C.
- Rationale: Mass transport coefficients typically double for every 10 °C. Temperature changes directly affects mass absorption into the contact sampler.
- Rationale: Contact masses may have significant thermal mass. Conducting tests without preheating masses may result in an inaccurate contact test temperature and variable mass absorption.

Contact Test Touch Time: The core contact test touch time is 15 minutes ± 45 seconds. If other touch durations are used the contact test touch time should be within ± 5% of the target total touch time.

- Rationale: The contact test result will vary with the contaminated surface area and touch length of time. For non-sorptive surfaces, the majority of mass adsorbed by the contact sampler is likely to occur within the first minute and is less affected by time. The contact touch time duration is directly proportional to contact test result for sorptive surfaces.

Contact Test Pressure: The core test contact test pressure is 0.7-1.0 psi (0.05-0.07 kg/cm^2), unless specified differently by test sponsor.

- Rationale: The pressure exerted on the contact sampler will determine the degree of contact between the contact sampler and the coupon. The contact sampler is usually a 'soft' material (i.e., low durometer) and will deform when pressure is applied. When more pressure is applied, the contact sampler will deform and increase the microscopic contact area due to 'filling in' the microscopic surface roughness of the sample and contact sampler. Increasing the pressure will increase the contact area which will increase mass absorption in the contact sampler. This has been documented in work by Schwope.
- Note: contact condition (wet vs. dry) has the same effect. If the coupon is wet, the water will 'fill in' the microscopic surface roughness and result in an increase in mass absorption in the contact sampler and may alter mass transport mechanisms.

Contact Sampler: The contact sampler is a simulant for human skin. The only guidance for material selection at this time is latex dental dam. The comparison of data using different contact sampler material may not produce similar results limiting direct comparison of test data.

- Rationale: The contact test is supposed to measure the mass of agent that would be transferred to skin. The mass of agent transferred to the contact sampler is a function of mass transport phenomenon that are material dependent (see EPA/600/8-91/011B 1992, *Dermal Exposure Assessment: Principles and Applications*). Materials with different mass transport properties will yield different mass absorption results. Comparison of contact results using different contact sampler materials is not advised.
- Note: the absorption rate of a contact sampler (skin or latex) is specific to the transport properties of the contaminated material, agent, and contact material. There is the possibility that skin and latex may have similar absorption rates on one material, but not on another.
- Note: The use of dental dam is recommended, though there is currently no published report characterizing the difference between this material and skin transport from various materials.

REVISION HISTORY

March 2008: original document in source document format. Based on TOP 8-2-061, 2002 initial release.

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Test Procedure 6-E: Panel (Coupon) Extraction Method to Determine Remaining Agent

SUMMARY OF PROCEDURE

The coupon extraction is the measure of the agent present in and on the test material after the decontamination process that could pose a future unknown hazard. The coupon is extracted in solvent, and the extract solution is analyzed. This procedure requires the collection and analysis of the rinse water. Dose-confirmation samples_are used to measure the delivered mass. Rinsate must be analyzed to determine the amount of agent physically removed if percent neutralization is calculated. **This procedure is recommended for the determination of percent neutralization and reduction in starting challenge.** This method can be used to evaluate decontaminant performance against liquid-phase contaminants such as chemical-warfare agents, chemical-warfare agent simulants, toxic-industrial-chemicals, and toxic-industrial-materials. The terms contaminant and agent are used interchangeably.

This procedure provides the following information:

- The mass of agent in nanograms recovered from the coupon after the decontamination process.
- This test may also provide the mass of agent by-products in nanograms recovered from the coupon if the appropriate analytical methods are used.

The following prerequisite tests are required for this test procedure:

- Procedure 6-C, "Rinsate Analysis for Agent Test Method" is the measurement of the amount of agent physically removed from the coupon during the decontamination process.
- Procedure 6-F, "Panel (Coupon) Extraction Efficiency Test Method" is the method for determining the efficiency the selected solvent has for recovering agent from the coupon.
- Procedure 6-H, "Chromatographic Analysis Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

This procedure alone does not provide the complete assessment of the decontaminant's performance for reducing the agent contamination or reporting the hazard. The complete assessment of a decontaminant performance should also address:

- Reporting **percent neutralization, percent efficacy,** or **reduction in starting challenge** in g/m^2.
  - Procedure 6-G, "Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy, or Reduction in Starting Challenge" is the process for converting the mass of agent recovered from the contact sampler to a reported hazard value.

Limitations:

- This test procedure cannot be used to calculate a contact- or vapor-hazard reported value.
- **Contaminant Simulant:** Chemical compounds for chemical agents are often used during early screening or at non-chemical agent surety facilities. A chemical agent simulant is a chemical compound of lower toxicity than the chemical agent with at least one property similar to the chemical agent, such as certain bonding, functional group, physical property, etc. Simulants should be selected based on the main property being tested for the most accurate

comparison. Since simulants do not contain all of the same physical and chemical properties of the live agent, simulant data alone is not sufficient to determine decontaminant performance. It is recommended that the simulant performance be confirmed with agent data.

- This test can only be conducted on coupons as extraction is required (i.e., small items). Coupon size must be small so that the coupon can be fully immersed in solvent. The extraction of large panels requires additional solvent resulting in a lower extractant agent concentration which places additional burdens on the required analytical equipment 'sensitivity'.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA). In this case, the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample** – the liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **breadboard, brassboard, prototype** – technology in differing degrees of configuration still under development that is not in final form. This can apply to test fixtures, formulations, and/or the decontamination system / applicator.
- **chemical agent** - a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contact hazard -** the amount of contaminant remaining on the surface that, based on toxicological human estimates, could pose a threat to unprotected personnel touching the contaminated surface.
- **contaminant -** a chemical compound with harmful effects to humans that is to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemicals, and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than one drop.

- **coupon** - test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in. diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** – the treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant** - for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process** - the process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically, for these procedures the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing, and drying.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – a sample the providing mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer's specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency** - the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **hazard** - A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*
- **moderate condition** - the test condition in the middle of the testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization** - the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption though there may be a minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive

with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.

- **operational decontamination** – decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material, and/or working areas in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **percent efficacy (and calculation)** - the measurement of the amount of contaminant removed from the material of interest as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **percent neutralization (and calculation)** - the measurement of the amount of contaminant reacted/neutralized as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **reduction in starting challenge (and calculation)** – the measurement of the mass of contaminant that has been removed from the material of interest. This is the calculation most often employed for the evaluation of physical removal, sorbent, or pre-clean techniques. The value can be reported as calculated, approximated, or inferred.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **remaining agent** - the amount of contaminant present in / on the material of interest after the decontamination process has been conducted. This value is different from the residual agent in that no mass has been removed from the coupon by contact or vapor testing. This value cannot be used to calculate a contact- or vapor-hazard.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **rinsate** - the collected rinse from the decontamination process. Sample may include residual decontaminant, agent, or agent byproducts in water.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface it is better described as a thin film.
- **sorptive / Porous Materials** - a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.

- **test condition** - for a specific agent – material- decon set the combined contamination, aging, decontaminant process, environmental, and test sampling process (i.e., contact, vapor, remaining, residual) variables.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
  - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
  - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agents, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of the live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
  - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Decontaminants:** The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid-, or vapor-phase, and may contain a reactive functionality for neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Extraction solvents:** The test requires the extraction of sorbed agent from test materials such as the contact sampler and/or coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride, and solvent blends.
- **Water:** Decontamination processes typically involve a post-rinse step and some decontaminants are made using water. Laboratory testing will use distilled or deionized water unless otherwise instructed by the test sponsor

EQUIPMENT

The equipment required for this method includes tools for delivering contaminant, decontaminant, and rinse water; maintaining environmental control, and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision, and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter contamination area.

- **Contaminant Delivery Tool:** The tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (µL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. For example, the core coupon test specifies using a total contamination volume of 2 µL delivered as two 1 µL drops for a 1 g/m^2 starting challenge.
  - <u>Pipette</u>: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. These are also best suited for pipetting volatile liquids. The smallest delivery volume, based on a survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
  - <u>Syringe</u>: The positive displacement tool best suited for the delivery of smaller drop volumes. The smallest delivery volume, based on a survey of commercial items with repeater capability, is about 0.2 µL.. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
  - <u>Computerized Dispensing System</u>: A automated tool with the ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.
- **Decontaminant Delivery Tool:** The tool used to deliver a specific volume of decontaminant to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The core coupon test

specifies using a decontaminant volume of 0.100 to 1.00 mL. The specific decontaminant under evaluation may use other delivery volumes.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of decontaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.

- Spray Bottle: Some applications will mimic a spray application using a spray bottle. The tool should be evaluated to determine the number of pumping actions required to achieve target decontaminant application. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and exact usage should be documented.

- Developmental Breadboard, Brassboard, or Protoype Technology: These are technologies under development that are not in their final configuration. The decontaminant generation and delivery may not be known. Tools obtained or developed by the testing laboratory which has no performance specification standards or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and exact usage should be documented.

- Vendor Provided Technology: This is equipment provided from vendor that may be breadboard, brassboard, prototype, or commercial in configuration. The technology is operated per vendor guidance. Tools obtained or developed by the testing laboratory which has no performance specification standards or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and exact usage should be documented.

- **Water Rinse Delivery Tool:** The tool for the delivery of specific volumes of water to the coupon surface to remove decontaminant from the surface. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. It is recommended that the tool used has the ability to control the flow rate in order to reduce operator-to-operator variations. The typical delivery volume for a 2 in. diameter circular contamination area range is 60 mL.

    - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. An example is the Dispensette and Brinkman brands. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.

- Pump: These are other precision liquid dispensing systems. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test. Tools obtained or developed by the testing laboratory which have no performance specification standards or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and exact usage should be documented.

- **Extraction Solvent Delivery Tool:** The tool used for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
- **Sample Dilution and Analytical Standard Preparation Tools:** These are the tools used to prepare sample dilutions. The tools must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
  - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.
- **Environmental Chamber:** This is a temperature and relative humidity controlled chamber for the preconditioning and aging of coupons. The fixture should be able to maintain test specific environmental conditions (e.g., temperature and relative humidity) even when adding or removing samples. The system must have temperature and relative humidity data logger capability, be able to store and download temperature and humidity data and traces to a computer for further analysis. The system must be able to maintain temperature and relative humidity. The system operation and range should be known.
- **Contaminated Area Measurement:** This is a fixed-site photographic setup to visually capture the agent contamination surface area coverage after dosing, aging, and any other critical steps in the decontamination process. A photograph

resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation.

- Digital Camera on Fixed Stand
- Imaging Station

- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Method 6-H. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically is used to line work space, and to protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Coupon(s):** test sample representative material surface.
- **Coupon tray:** optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains an excess volume of household bleach in order to submerge items.
- **Extraction containers**: The procedure involves the extraction of the contact sampler and/or coupon. A glass container such as a vial or jar of sufficient size to hold both the contact sampler and/or coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon is preferred, in order to prevent extraction of plasticizers or other impurities into the sample. The use of plastic containers is not recommended for chemical agent testing.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** typically used during the aging step to cover the coupon surface to minimize evaporative loss. These can also be used as a sample holder.
- **Rinsate collection container:** If rinse water analysis is required, the rinse should be collected in a glass container of sufficient volume for the rinse water and extraction solvent, preferably a wide mouth jar. It is recommended to limit the use of funnels or other tools that may uptake agent during collection. The use of plastic containers is not recommended for chemical agent testing. The container cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers, or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks, and writing utensils.

- **Timing device(s):** The test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Transfer pipettes**
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, and a pH meter.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state, and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health, and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.

This test has Options A, B, and C that are step variations based on potential variables that could be explored. The core test evaluation is designated by Option A. This option is based on a liquid decontaminant tested at moderate environmental conditions using equipment with known accuracy. This option should be used unless otherwise instructed by a test sponsor. Option B is similar to Option A, but allows for different parameters, such as temperature. Option C is designed for the evaluation of new technologies or the use of conditions outside of the core test. The use of lettering does not indicate a test grade. The letter serves as a quick reference to the selections made during testing and the considerations required for comparing different groups of data. Optiosn A and B parameter choices are preferred in cases where lab-data must be compared to requirements; however, Option C parameters may need to be used, especially for the evaluation of new technologies.

This test has Options 1 and 2 for the positive- (contaminant, no decontaminant) or negative- (no contaminant, decontaminant) control, respectively. This test aligns with test procedure 6-E primary test (Option A, B, C) requiring the use of the identical test process used.

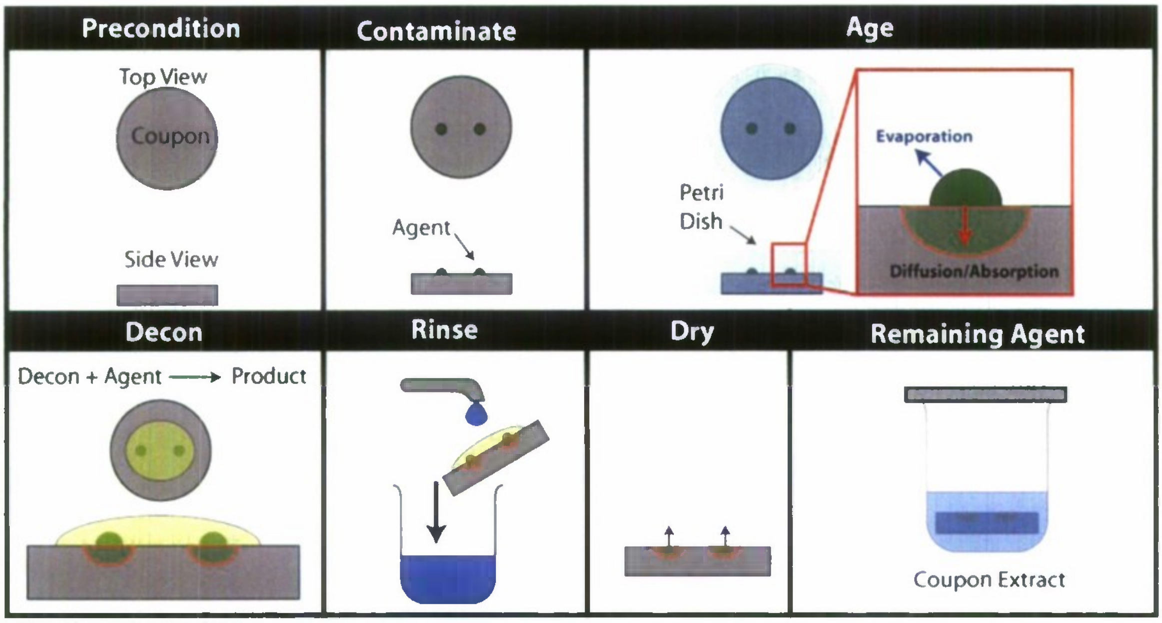

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Figure 6E-1. Remaining Agent Test Representation.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to the start of the test. Preparation tasks for this method may include:

- **Identify the calculation desired: remaining agent, percent neutralization, percent efficacy, reduction in starting challenge. Review the Calculation Method 6-G and select the appropriate test methods and options within a test method to ensure the necessary data is collected.**
- Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars), and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Decontaminant preparation.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- It is recommended that the contaminant equilibrates to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case, it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, rinse, and contact test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of five coupons per test condition and three dose-confirmation samples per contamination set.

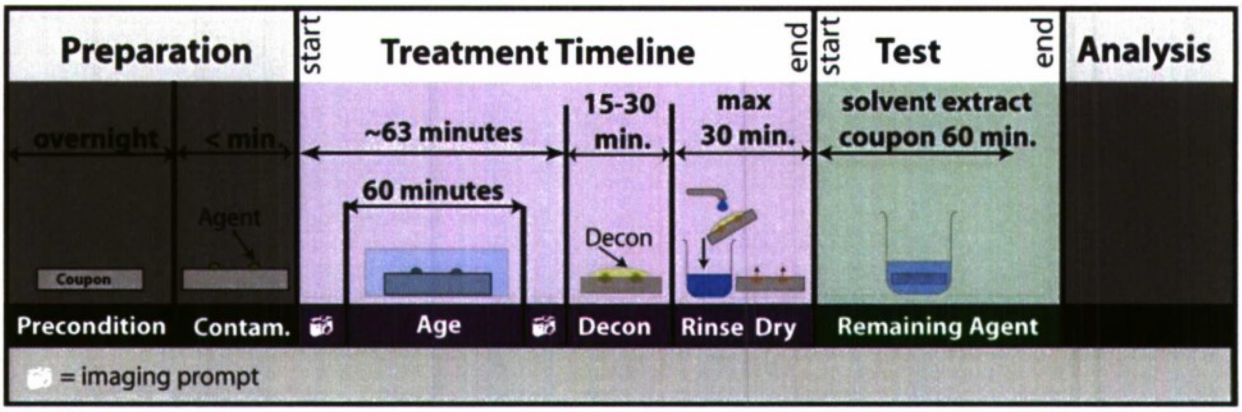

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Figure 6D-2. Remaining Agent Test Timeline Representation

2.0 Precondition Coupons

2.1 Set the environmental chamber to the specified test condition

OPTION A (core test): **moderate condition** test using the environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported.

OPTION B (core test, variable condition): variable condition test with the environmental chamber using the test sponsor / director temperature and relative humidity set-point. The most common test cases are high and low temperature and relative humidity.

OPTION C (outside core test): The test is conducted at room conditions without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate, or cold.

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupon conditioning is performed using the same method including temperature, relative humidity, location, and time as that used in procedure 6-E primary test (option A, B, C).

OPTION 2 - Negative Control (no contaminant, decontaminant): the coupon conditioning is performed using the same method including temperature, relative humidity, location, and time as that used in procedure 6-E primary test (option A, B, C)

2.2 Allow the environmental chamber to equilibrate at the set-point temperature and relative humidity. The time to reach set-point equilibration may vary based on equipment and set-point conditions. It is recommended that the temperature and humidity are maintained at the set-point for at least 30 min. prior to the start of conditioning.

2.3 The coupons are placed horizontally on coupon trays with the test surface to be contaminated / decontaminated facing upwards.

2.4 Once the chamber has equilibrated at the set-point temperature and relative humidity, place the trays into the environmental chamber for at least 60 min. The recommended practice, if possible, is to precondition the test materials overnight.

- Note: Some materials may require special preconditioning treatments. For example, cellulose based materials and concrete contain significant moisture. These types of materials do not typically achieve

moisture equilibrium in less than 24 to 48 hours. Longer precondition times may be required for certain materials. An example procedure for wood is ASTM D4442.

2.5 Samples should not be removed until ready to execute step 3 contamination.

2.6 Complete the required reporting for this section.

3.0 Contaminate Coupons

3.1 Identify the contamination density to include number of drops, drop volume, and deposition pattern.

OPTION A (core test): Contamination density is 1-1.2 g/m^2 applied using pipette / syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): Variable contamination density is typically between 1 to 10 g/m^2 applied using pipette / syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

OPTION C (outside core test): The application of agent using brushes, rollers, or sprays applicators such that the amount of agent applied to the specific surface is not tightly quantifiable. Note: The calculation of percent neutralization might not be feasible using this option.

OPTION 1 – Positive Control (contaminant, no decontaminant): The coupon contamination is performed using the identical process used for the procedure 6-E primary test (option A, B, C) testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): Contaminant is not applied.

3.2 Set tool to the appropriate drop volume

- Note: The pipette volume should not be changed within a set of procedures. Tests have shown that changing the tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with a clean, appropriate pipette tip

3.4 Load the contaminant delivery tool in accordance with manufacturer's directions

3.5 Deliver to the surface the appropriate number of drops to achieve the contamination density. Reload the tool and repeat as needed for the total number of coupons. Treatment time starts after the coupon is contaminated. The use of timing charts is recommended for multiple samples.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests), or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.6 If using pipettes or syringes to deliver the contaminant, prepare the "dose confirmation" sample. At least three replicate samples are recommended.

3.6.1 Deliver to a scintillation vial the appropriate number of drops to achieve the contamination density.

3.6.2 Add 20 mL of extraction solvent.

3.6.3 Cap vial

3.6.4 Thoroughly mix contents by inverting vial three times.

3.7 Observe the post-contamination drop interaction with the surface and surface coverage.

OPTION A (core test): Using a digital camera or imaging station, photograph each coupon surface. A photograph resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation.

OPTION B (core test variable condition): some materials may not allow for the rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three independent coupon replicates should be carried through the test process and treated to enable digital photography. A photograph resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation.

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OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered is documented both in words and hand drawing.

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical process used for the procedure 6-E primary test (option A, B, C) testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied, skip to step 5.

3.8 Cover coupons with a Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

3.9 Complete the required reporting for this section.

4.0 Coupon Aging

4.1 Coupons are aged.

OPTION A (core test): Coupons are aged in environmental chamber for 60 min at a moderate condition test with the environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. The environmental chamber should have logging capability for real-time temperature and humidity recording.

OPTION B (core test, variable condition): Coupons are aged in an environmental chamber under one or more of the following cases. The environmental chamber should have logging capability for real-time temperature and humidity recording.

- Variable temperature and relative humidity: aging is conducted at test sponsor / director designated temperature and relative humidity.
- Variable aging time: shorter aging time for immediate or operational decon applications, or aging period longer than the option A basic thorough test. The aging may be at the moderate condition and/or variable temperature and relative humidity.

OPTION C (outside core test): The test is conducted at room conditions without the use of an environmental chamber. Note: Room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

OPTION 1 – Positive Control (contaminant, no decontaminant): The coupons are aged using the identical procedure as the procedure 6-E primary test (option A, B, C) testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): skip to step 5.

4.2 Observe the post-aging drop interaction with the surface and surface coverage. (If no aging period is used, this step can be skipped).

OPTION A (core test): Using a digital camera or imaging station, photograph each coupon surface. A photograph resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation. There is a chance for some materials the post aging image may not be visible without use of color indicator or dye.

OPTION B (core test variable condition): Some materials may not allow for rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three coupon replicates should be carried through the test process and treated to enable digital photography. A photograph resolution of 9 – 25 pixels per droplet measured is recommended for the surface area calculation.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered documented.

OPTION 1 – Positive Control (contaminant, no decontaminant): The identical process used for the procedure 6-E primary test (option A, B, C) testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): Contaminant is not applied.

4.3 Complete the required reporting for this section.

4.4 Coupons are moved to decontamination test area at end of aging period.

5.0 Pre-rinse the Coupons

5.1 Coupons are rinsed.

OPTION A (core test): pre-rinse is not used for the core test.

OPTION B (core test variable condition): Pre-rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for processing and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION C (outside core test): The use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water also falls outside the core test, as the rinse evaluation method needs to be completed to determine the impact of surfactants on accurate agent measurement.

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

5.2 Complete the required reporting for this section.

6.0 Decontaminate the Coupons

6.1 Apply decontaminant

OPTION A (core test): For the core test there are a few sub-options based on the test objective. The decontaminants are liquid-phase and applied using a pipette. Dispensettes or pumps may fall under Option A if the decontaminant delivery volume to the contaminated region can be accurately measured. Unless otherwise specified, the decontaminant applied is typically at room conditions. The amount of decontaminant applied is based on the following guidance.

- Option A-1: For early research tests, it is recommended that 1.00 mL of decontaminant is evenly dispensed over the contaminated coupon surface in a single application. Care should be taken to ensure that the decontaminant is delivered uniformly over the test area. This recommended decontaminant volume is for starting challenges in the 1 to 10 g/m^2 range to ensure that decontaminant covers the contaminated surface area. Some agent-material interactions could result in significant contaminated surface coverage that smaller decontaminant volumes may not be able to adequately cover the entire contaminated surface yielding data scatter due to decontaminant delivery.
- Option A-2: FM 3-11.5 recommends a decontaminant to contaminant ratio of 50:1. This corresponds to 0.100 mL to 1.000 mL for a 1 to 10 g/m^2 starting challenge, respectively.

OPTION B (core test variable condition): Some liquid-phase decontaminants may require applying more or less decontaminant. For vapor-phase decontaminants, apply the appropriate fumigant concentration.

OPTION C (outside core test): The use of solid decontaminants, sorbent wipes, brushing, or mechanical scrubbing methods are outside the scope. These materials have the potential to retain or physically relocate agent. The use of these methods requires adjustment in order to calculate percent neutralization. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes falls here. Decontaminant is applied as best as possible in accordance with the technology operating procedures.

OPTION 1 – Positive Control (contaminant, no decontaminant): decontaminant is not applied.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in procedure 6-E primary test (option A, B, C) should be used here.

6.2 Cover coupons with a Petri dish (or equivalent cover) to minimize cross contamination and evaporative loss.

6.3 Wait the appropriate decontaminant residence time at the specified environmental conditions.

OPTION A (core test): Standard decontaminant residence time is from 15 to 30 min for liquid-phase decontaminants in an environmental chamber at an ambient condition test

with the environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant data scatter. Relative humidity should be measured and reported. Environmental chamber should have charting capability for real-time temperature and humidity logging.

OPTION B (core test variable condition): liquid-phase decontaminants outside the 15 to 30 minute range or at variable temperature or humidity that are placed in an environmental chamber for residence period.

OPTION C (outside core test): liquid phase decontaminants evaluated at room condition. Sorbents and wipes may have other residence times on surface. Vapor-phase decontaminants may dictate environmental conditions as part of the process. Breadboard, Brassboard, Prototype, or vendor provided equipment with specified application processes using residence times outside the core 15 to 30 min or environmental conditions outside specified test conditions fall here.

OPTION 1 – Positive Control (contaminant, no decontaminant): The baseline study uses selected procedure components to those used in procedure 6-E primary test (option A, B, C). The identical decontaminant residence time, temperature, and relative humidity should be used. If the decontaminant process utilizes air movement (i.e., vaporous decontaminants), the identical process parameters and decontaminant residence time are used.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in procedure 6-E primary test (option A, B, C) should be used here.

6.4 Complete the required reporting for this section.

7.0 Post-Rinse and Dry

7.1 Coupons are rinsed.

OPTION A (core test): The rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in a glass jar for processing and analysis under Method 6-C. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, or front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION B (core test variable condition): Rinse is not collected or analyzed.

OPTION C (outside core test): The use of pressure washers falls outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time, hot soapy water also falls outside the core test as the rinse evaluation method needs to be completed to determine impact of surfactants on accurate agent measurement. Some decontaminants do not require a post rinse. The impact of residual decon on the contact test analytical measurements must be evaluated.

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

7.2 Coupon drying

OPTION A (core test): Passive drying is recommended at room conditions, preferably in a chemical fume hood (or equivalent) with approximately 100 linear feet per minute (lfm) airflow. The coupons are recommended to be placed at an angle to increase the air flow over the surface. Coupons should not be dried for more than 30 min. Residual water on the surface should be noted. For most applications, wicking the last bead of rinse water should have little impact on the results.

OPTION B (core test variable condition): Controlled air drying which is an active blowing with established air temperature, flow rate, etc.

OPTION C (outside core test): Blotting, wiping, or other direct surface contact methods that may also remove agent as part of the process. These methods can impact contact measurement. No drying would also fall here as residual water affects the contact measurement if trying to conduct the dry-skin equivalent contact test.

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 6-E primary test (option A, B, C) should be used here.

7.3 Complete the required reporting for this section.

7.4 The coupon treatment process is considered complete once the surface of interest has dried or the 30 minute dry time has elapsed. The contact test time is then initiated. (Figure 6D-3).

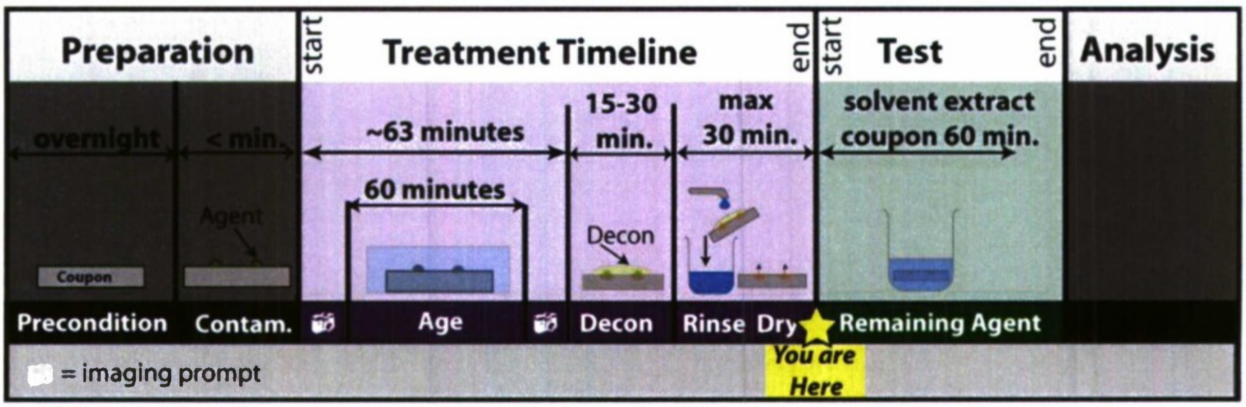

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Figure 6E-3. Remaining Agent Test Timeline Representation.

8.0 Remaining Agent Test

8.1 The coupon is extracted for remaining agent.

8.1.1 Place the coupon in an extraction jar. For most materials, the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

8.1.2 Add 20.0 mL of extraction solvent ensuring coupon is completely immersed.

8.1.3 Place a PTFE/ Teflon-lined lid on extraction jar.

8.1.4 Swirl the jar

8.1.5 Coupon will remain in the extraction solvent for 60 min. Note: other extraction times can be used. The extraction efficiency measured in Method 6-B must use the same extraction time.

8.1.6 At the end of the coupon extraction period, swirl the jar, open the vial, and, using a clean pipette tip, place a sample into an analytical vial for analysis.

8.2 Complete the required reporting for this section.

9.0 Chromatographic Analysis for Agent

9.1 Samples are analyzed based on guidance in Procedure 6-H. This test generated three types of samples for analysis

- Dose confirmation
- Coupon extract for remaining agent

9.2 Sample dilution may be required for samples to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

9.3 Obtain a list of analytical results in ng/mL which already accounts for any additional dilutions.

9.4 Complete the required reporting for this section.

10.0 Perform Calculations

10.1 Obtain the analytical results for

- Dose confirmation
- Coupon extract for remaining agent

10.2 Perform calculations.

10.3 Report for this section

- Extraction efficiency corrected remaining agent coupon test results in ng

CALCULATIONS

1.0 Convert Results from ng/mL to ng

1.1 Obtain the chromatography data in ng/mL for the coupon extract for the remaining agent (**RA_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between the sample collection and analysis.

1.2 Convert the coupon extraction result from mass in solution (**RA_E**) to mass (**RA_M**)

For each contact sampler extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{RA_M} \text{ (in ng)} = \mathbf{RA_E} \times \mathbf{EV} \qquad (1)$$

1.3 Calculate 'Analyte Mass Delivered' ***Del*** from the dose confirmation sample

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL. Average the results for the replicates reporting the standard deviation

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

2.0 Calculate the remaining agent test results corrected for extraction efficiency

2.1 Obtain the calibration curve developed from Procedure 6-B.

2.2 Calculate the extraction efficiency corrected remaining agent test result ($\mathbf{RA_C}$) in ng using the equation identified in step 4.0 of procedure 6-B.

3.0 Complete the required reporting for this section

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Decontaminants:** Provide for each decontaminant used the decontaminant name / description, source, date of preparation, purchase or expiration date (as applicable). Include a description of the preparation process for materials requiring pre-use preparation such as dilution or mixing.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.
- **Water:** Provide a description of the water used and source for each use of water. For example, laboratory distilled water may have been used to mix the decontaminant and certified ocean seawater might have been used for the rinse. The water reporting would include the description for both the decontaminant prepared and rinse waters used. Include characterization data / specification sheet details for any certified or specialty water used.

EQUIPMENT

- **Contaminant Delivery Tool**
  - Tool identification including manufacturer, model number, and volume dispensing range.
  - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
  - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
  - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Decontaminant Delivery Tool**
  - *See contaminant delivery tool listing for pipettes and syringes.*
  - For breadboard, brassboard, and prototype equipment, provide a description of the decontamination system including configuration and identification number / name.
  - For vendor provided equipment, provide the vendor name, item description, and model number.
- **Water Rinse Delivery Tool:** see *contaminant delivery tool listing.*
- **Extraction Solvent Delivery Tool:** see *contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Temperature Controlled Surface for Contact Test**: include tool identification including manufacturer and model number, and tool performance specifications if available.
- **Environmental Chamber:** Provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems. If a data logger is used, then include the data logging frequency.
- **Contaminated Area Measurement (if performed)**: include tool identification including manufacturer and model number, camera resolution, description of area measurement calculation and associated error with calculation if known.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Precondition Coupons**

- Option used (A, B or C)
    - For Option C: a description of how the conditioning was performed.
- Precondition length of time with units of hours and minutes.
- Temperature average with standard deviation, high, and low for conditioning period.
- Relative humidity average with standard deviation, high, and low for conditioning period.
- Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.

- **Contamination**
    - Option used (A, B or C)
        - For Option C: a description of how the contamination was performed.
    - Contamination density in g/m^2.
    - Total agent volume in microliters (μL) per coupon.
    - Agent drop volume size(s) in microliters (μL) per coupon.
    - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
    - Test location temperature and relative humidity during contamination.
    - Contaminant temperature at time of contamination.
    - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (μL) per vial, the agent drop volume size(s) in microliters (μL) per vial, the solvent identification, and the solvent volume.
- **Post-Contamination Surface Contamination Observation**
    - Option used (A, B or C)
    - Written description of applied drops as they appear for each coupon (e.g., sessile, spread).
    - For Option B: how contrasting was achieved.
    - For Option A/B: provide a representative photograph
    - For Option A/B: provide the calculated contaminated surface area
    - For Option C: provide a hand drawing of the representative contaminated area, estimated contaminated surface area, and the method for estimating contaminated surface area.
- **Aging**
    - Option used (A, B or C)
        - For Option C: a description of how the aging was performed.
    - Coupon cover description including source, part number, size, and volume.
    - Aging length of time in units of minutes.
    - Temperature average with standard deviation, high, and low for aging period.
    - Relative humidity average with standard deviation, high, and low for aging period.
    - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Post-Aging Surface Contamination Observation:** *see requirements for Post-Contamination Surface Contamination Observation.*
- **Pre-Rinse**
    - Option used (A, B or C)
        - For Option C: a description of how rinsing was performed.
    - Rinse material identification (i.e., distilled water, hot soapy tap water, etc.).
    - Rinse material temperature
    - Test location temperature and relative humidity during rinsing.
    - Total volume applied

- Description of the force and rate rinse applied

- **Decontamination**
  - Option used (A, B or C)
    - For Option C: a description of the decontamination process.
  - Description of the decontaminant application process.
  - Decontaminant temperature.
  - If decontaminant is applied "cold" or "warm" provide a description of how decontaminant was chilled or warmed.
  - Record amount of decontaminant applied
    - For liquids, volume delivered
    - For solids, mass delivered
    - For vapors, injection rate, flow rate, fumigant concentration, temperature, and relative humidity
    - Or other specifications per manufacturer's delivery instructions.
  - Coupon cover description including source, part number, size, and volume.
  - Decon residence time on coupon surface in minutes
- **Post-Rinse:** see *requirements for Pre-Rinse.*
- **Drying**
  - Option used (A, B or C)
    - For Options A, B and C: a description of how drying was performed.
    - For Option C: if no drying was used, provide a detailed description of how wet the surface was (representative photograph recommended).
  - Drying time in minutes
  - Description of drying location
    - If hood, specify air velocity
    - If flow chamber, specify flow rate and air temperature.
  - Temperature
  - Relative humidity
  - Description of any residual water on surface at the end of the drying period.
  - Detailed description of drying process used.
- **Remaining Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the remaining agent test results in nanograms per coupon and "dose confirmation" sample mass in nanograms.
- **Calculation Reporting Criteria**
  - Summary data table containing the following information. Some data may not be available based on procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
    - Data in nanograms per milliliter for the coupon remaining agent (**RA_E**) and the dose-confirmation samples (DCE) that have been corrected for any dilutions performed between the sample collection and analysis.
    - Remaining agent mass results (**RA_M**) not corrected for extraction efficiency in nanograms.
    - Delivered mass results (***Del***) in nanograms.
    - Extraction efficiency corrected remaining agent mass results (**RA_C**) in nanograms.
    - Test set (combination of test replicates) averages and standard deviations for data sets specific to reporting results for test objective(s).

- Summary of the coupon extraction efficiency determination (Procedure 6-F) for each agent – material - extraction solvent combination if Procedure 6-F was not directly executed and reported for this test report.
  - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
- Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the Amount of Contaminant Delivered in order to determine the difference. The Amount of Contaminant Delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Aging Temperature and Relative Humidity: Core test moderate condition is 21 ± 3 °C, preferred, ± 5 °C maximum. Aging temperature in general is target temperature ± 5 °C. No criterion for RH is specified, however, a test sponsor may specify depending on test objective.

- Rationale: Changes in temperature directly affect the amount of contaminant absorbed into a material. Any deviation in temperature increases the amount of error in the end test result. Therefore, deviations in temperature must be minimized. For example, mass transport coefficients typically double for every 10 °C increase in temperature.
- Rationale: Relative humidity is expected to have a minor influence on test results compared to other system variables.

Aging Time: Core test aging time is 60 ± 3 min. For other aging times, the acceptance criterion is target time ± 5%.

- Rationale: The more or less time a contaminated coupon is aged, the more or less contaminant is absorbed into the coupon. For example, mass adsorbed for sorptive non-porous materials (based on Fick's first law) is proportional to square root of the aging time. A 5% time deviation could result in a 2.5% variation in mass absorbed into the coupon.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Amount of Decontaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered. In the event these criteria were not met, a repeatability study could be performed to determine the precision of the tool.

Decontaminant Residence Time: The total decontaminant residence time should be within ± 5% target time.

- Rationale: The measurement of the effect the decontaminant has for contaminant reduction is the main objective of the test. The decontaminant–contaminant interaction time will be proportional to the amount of agent removed and or neutralized, likely in a nonlinear manner.

Contaminated Surface Area: The contaminated surface area for a test set should have a small variance, although contaminant spreading on a material surface is a function of material-agent interactions. A large variance in the contaminated surface area could give false sense of test error; the cause of the variability should be investigated to determine if the data is acceptable. It is recommended to investigate if the variance in spreading is a property of the material-agent interactions or if it was a result of test procedures. If it was a result of test procedures the test should be rerun.

- Rationale: For sorptive materials the mass absorbed is proportional to the contaminated surface area (absorption is a flux-based process).
- Rational: For the contact test result, the agent mass sampled will be proportional to the contaminated surface area. The proportionality (e.g., square root area, linear area, area squared) is dependent on material properties and agent-material interactions.
- Note: The contaminated surface area immediately after contamination is likely to have little variation, however some material-agent combinations will result in spreading as a function of time, thus the pre-decon contaminated area may show a significant distribution. The pre-decon contaminated area should be used as the value to compare contaminated surface areas.
- Note: For comparison of data with different contaminated surface areas it is recommended to compare data using a mass per unit of contaminated surface area value rather than direct mass comparisons.

REVISION HISTORY

March 2008: original method.

Test Procedure 6-F: Panel (Coupon) Extraction Efficiency Test Method

SUMMARY OF PROCEDURE

The coupon extraction efficiency test method determines the amount of agent that can be recovered from the coupon using a specific solvent and extraction time. The mass of agent extracted is compared to the mass originally delivered to enable the correction of analytical data based on solvent extraction efficiency for a given extraction time. Any loss in the system, such as evaporation, will contribute to lower the measured extraction efficiency value. The delivered mass (e.g., dose confirmation sample) must be accurately measured to calculate the extraction efficiency. **Dose-confirmation samples** are used to measure the delivered mass. The test covers a range of concentrations equivalent to 250 mg/m^2 down to **requirement levels**, which at the time of writing are approximately as low as 0.005 mg/m^2. These results are used to correct the reported residual agent mass value reported in Procedures 6-A and 6-D.

This procedure provides the following information:

- An extraction efficiency correction calibration curve for the correction of agent mass reported as a function of the solvent extraction efficiency for a given extraction time.
- This method should be performed when any major changed is made in the laboratory process. Major changes include, new material lot, change in extraction procedure (e.g., time, temperature, extraction volume), change in solvent (e.g., different solvent or change in solvent grade used).

The following prerequisite tests are required for this test procedure:

- Procedure 6-H, "Chromatographic Analysis Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

Limitations:

- For ultra-low dose levels, non-detect recovery masses may be observed giving the appearance of a low-extraction efficiency. The calculations for determining the extraction efficiency calibration curve account for this situation.
- An assumption of this procedure is that all mass lost is attributed to incomplete extraction. Care should be taken in executing the method to ensure minimal agent loss occurs due to evaporation (especially for more volatile compounds) and coupon handling.
- The extraction efficiency calibration curve should only be used for the contamination drop volume and deposition pattern tested for an agent–material–solvent combination. If other drop volumes, deposition patterns, or solvents are routinely used for an agent-material pair, then the extraction efficiency calibration curve should be generated for each drop volume, deposition pattern, agent, material, and solvent combination.
- The evaluation of reactive materials can create challenges for extraction efficiency measurements as neutralization may be occurring during the extraction process.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA). In this case, the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample** - liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **chemical agent** - a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contaminant -** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemicals, and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in. diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample – a** sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer's specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or

reduction in starting challenge that require accurate measurement of the starting contamination.

- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency -** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*
- **moderate condition** - test condition in the middle of the testing range that is the standard indoor office / laboratory condition at 19-21°C and 50-60% relative humidity.
- **neutralization -** the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption, though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **panel** – *see coupon.*
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **residual agent** - the amount of contaminant present in/on the material of interest after the decontaminant process and hazard test has been conducted.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface, it is better described as a thin film.
- **sorptive/porous Material -** a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition -** for a specific agent–material-decon set, the combined contamination, aging, decontaminant, environmental, and test sampling process (i.e., contact, vapor, remaining, residual) variables.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.

- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
    - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
    - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to a live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of the live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
    - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Extraction solvents:** The test requires the extraction of sorbed agent from test materials such as the contact sampler and/or coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride, and solvent blends.

EQUIPMENT

The equipment required for this method includes tools for delivering contaminant and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision, and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20

microliters (μL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 μL delivered as two 1 μL drops for a 1 g/m^2 starting challenge.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. These are also best suited for pipetting volatile liquids. The smallest delivery volume, based on a survey of commercial items with repeater capability, is about 1 μL.. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
- Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. The smallest delivery volume based on a survey of commercial items with repeater capability is about 0.2 μL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
- Computerized Dispensing System: Automated tool with the ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.

- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of a 2 in. diameter circular disk is 20 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on the liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred for work with

chemical contaminants in order to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.

  - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.

- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Method 6-H. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space, and protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains an excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the contact sampler and/or coupon. A glass container such as a vial or jar of sufficient size to hold both the contact sampler and/or coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon is preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommend for chemical agent testing.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** typically used during the aging step to cover the coupon surface to minimize evaporative loss. These can also be used as sample holder.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers, or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test forms, laboratory notebooks, and writing utensils.
- **Timing device(s):** The test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Transfer pipette**

- **Optional items:** Items that may be used includean analytical balance.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state, and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health, and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement, and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination, and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements. The extraction efficiency function determined by this method is valid for the tested material lot and extraction method used. Lot-to-lot variations in test materials may exist and should be verified.

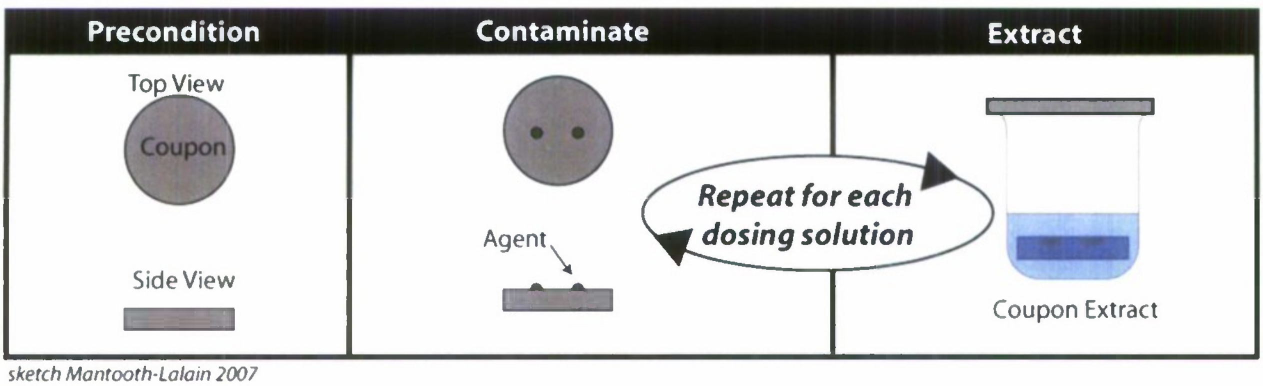


Figure 6F-1. Coupon Extraction Efficiency Test Sketch.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents, and analytical capabilities are available for the test. All equipment should be confirmed operational prior to the start of the test. Preparation tasks for this method may include:

- Turning on equipment that will need to thermally equilibrate (i.e., slidewarmer, environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars), and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.

- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- It is recommended that the contaminant equilibrates to room temperature prior to its use.

This procedure can be applied to multiple coupons during a single test session. In that case, it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, rinse, and contact test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of 5 coupons per test condition and 5 dose-confirmation samples per contamination set.

The test is performed at the conditions at which the extraction will occur

2.0 Prepare Dosing Solutions

2.1 Up to seven dosing solutions are prepared to provide various delivered mass values. Identify the smallest mass on the surface of the test material (e.g., coupon, dental dam) for the following two situations.

2.1.1 Multiply the smallest requirement surface concentration by the surface area of the test material to calculate the mass on coupon (e.g., JPID 2003 objective for VX is 0.005 mg/m^2 x 0.00202 m^2 x 10^6 ng/mg = 10.1 ng on coupon). Divide the mass on coupon by 10.

$$Mass_{\text{Requirement}} = \frac{\text{Requirement} \cdot \text{Surface Area}}{10} \cdot 10^6$$

2.1.2 The second situation to consider is the detection limit of the analytical method. Multiply the LOQ (ng/mL) of the most sensitive analytical method used (e.g., the LOQ of 0.05 ng/mL for VX on LC-MS/MS) by the extraction volume (mL) as defined by

$$Mass_{\text{Analytical}} = LOQ \cdot Volume_{Extract}$$

2.1.3 The value $Mass_{Min}$ is defined as the smaller of $Mass_{Requirement}$ or $Mass_{Analytical}$.

Note: If $Mass_{Requirement}$ is less than $Mass_{Analytical}$, this implies that the analytical quantitation limit cannot detect an order of magnitude below the requirement.

2.2 Determine the mass of the contaminant to deliver to the coupon

2.2.1 The selection of masses to be delivered is based on the fitting of the empirical EE models. The following guidance will deliver a model that should represent the system.

2.2.2 Calculate the mass to be delivered using the following table as guidance

2.2.3 Calculate the concentration of the solution to deliver the same contamination profile as used in testing (e.g., Procedures 6-A, 6-D and/or 6-F) to contaminate the coupon. For example, if two 1.0 µL drops are used to contaminate the coupon with neat agent for testing, use two 1.0 µL drops for this test. Solution concentration (ng/mL) can be calculated from the $Mass_{Delivered}$ (ng), number of drops (n), and drop volume (V in µL) as

$$\text{Sln. Conc} = \frac{Mass_{Delivered}}{nV \cdot 10^{-3}}$$

Guidance Formula	Example: VX $Mass_{Delivered}$ $Mass_{Min}$ = 1.00 ng	Resulting Nominal Solution Conc. (ng/ml) For 2 x 1.0 µL drops
$Mass_{Min}$ × 2	2	1,000
$Mass_{Min}$ × 5	5	2,500
$Mass_{Min}$ × 10	10	5,000
$Mass_{Min}$ × 33	33	16,500
$Mass_{Min}$ × 100	100	50,000
$Mass_{Min}$ × 1,000	1,000	500,000
$Mass_{Min}$ × 10,000	10,000	5,000,000

2.3 Prepare the dosing solutions

2.3.1 The solutions can be prepared either volumetrically or gravimetrically. The discussion here is for volumetric addition. This procedure could be scaled up to use volumetric glassware. The approach here was to reduce the total agent consumption and waste generated. An example solution preparation table for VX using an 89.5% pure neat agent is shown. Higher concentration solutions are prepared from neat agent, and then serially diluted to create lower concentration solutions.

Note: Extraction efficiency is determined from mass delivered which is measured by dose-confirmation samples (i.e., not solution concentration x dose volume). This approach minimizes any bias introduced by the dosing tool or solution preparation technique and reduces the accuracy required to prepare the dosing solutions.

2.3.2 The solutions are prepared by the placement of a set volume of solution dispensed via pipette into a vial to which the appropriate solvent of solvent is added via pipette.

2.3.3 The vial is immediately capped using a PTFE/Teflon lined cap.

2.3.4 The vial is inverted three times for thorough mixing.

Agent	**VX**
Density (ng/ml)	1,008,300,000
Mole % Purity	89.5%
Corrected Density	902,428,500

Standard Name	Nominal Conc (ng/mL)	Stock Solution	Volume Stock Sln (mL)	Solvent Volume (mL)	Total Vol (mL)	Corrected Conc (ng/mL)
SolutionA	50000000	Neat	0.059	1.000	1.059	50,276,942
SolutionB	5000000	SolutionA	0.112	1.000	1.112	5,063,865
SolutionC	500000	SolutionB	0.110	1.000	1.110	501,824
SolutionD	50000	SolutionC	0.111	1.000	1.111	50,137
SolutionE	16500	SolutionC	0.034	1.000	1.034	16,501
SolutionF	5000	SolutionD	0.112	1.000	1.112	5,050
SolutionG	2500	SolutionD	0.053	1.000	1.053	2,524
SolutionH	1000	SolutionE	0.065	1.000	1.065	1,007

2.4 Complete the required reporting for this section.

3.0 Contaminate Coupons

3.1 The contamination approach should match that used in the core test performed for Method 6-A. Identify the contamination density to include the number of drops, drop volume, and deposition pattern. Test Method 6-A Option C cannot be performed for this test as the amount delivered cannot be tightly measured.

OPTION A (core test): Contamination density is 1-1.2 g/m^2 applied using a pipette, syringe, or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): Variable contamination density is typically between 1 to 10 g/m^2 applied using pipette, syringe, or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

3.2 Set the tool to the appropriate drop volume

- Note:Tthe pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit the pipettor with a clean, appropriate pipette tip

3.4 Load the contaminant delivery tool with the dosing solution in accordance with the manufacturer's directions.

3.4.1 Place coupon into extraction jar.

- Note: Loading the coupon into the extraction jar is an attempt to minimize air flow that is expected in engineering controls. This action may minimize evaporative loss.

3.4.2 Deliver to the surface the appropriate number of drops to achieve the contamination density.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon,

adsorbent paper (M8 paper for surety tests), or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.4.3 Allow the solvent to evaporate, which is typically 5 to 20 seconds. Do not exceed 60 seconds.

3.4.4 Add 20 mL of extraction the solvent

3.4.5 Cap jar with a PTFE/ Teflon-lined lid.

3.4.6 Gently swirl the container to mix the contents.

3.4.7 The coupon will remain in the extraction solvent for 60 minutes. Note: Other extraction times can be used. The extraction time used here should agree with extraction time used for testing (e.g., Procedures 6-A, 6-D or 6-E).

3.4.8 Gently swirl the container to mix the contents.

3.4.9 Using a clean, disposable pipette, load the analytical vial with an aliquot of extractant solution.

3.4.10 Repeat steps 3.4.1 through 3.4.9 as needed for the total number of coupons.

3.4.11 Prepare the "dose confirmation" sample. At least five replicate samples are recommended.

3.4.11.1 Deliver to a scintillation vial the sample number of agent drops.

3.4.11.2 Add 20 mL of extraction solvent.

3.4.11.3 Cap the vial

3.4.11.4 Thoroughly mix contents by inverting vial three times.

3.4.11.5 Using a clean, disposable pipette, load the analytical vial with an aliquot of extractant solution.

3.5 Using a clean pipette tip, repeat steps 3.3 and 3.4 for each solution.

3.6 Complete the required reporting for this section.

4.0 Chromatographic Analysis for Agent

4.1 Samples are analyzed based on guidance in Procedure 6-H.

- Dose confirmation
- Coupon extract

4.2 Sample dilution may be required for the sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

4.3 Obtain a list of analytical results in ng/mL which already accounts for any additional dilutions beyond the initial extraction.

4.4 Complete the required reporting for this section.

5.0 Perform Calculations

5.1 Obtain the analytical results for

- Dose confirmation
- Coupon extract

5.2 Perform calculations.

5.3 Complete the required reporting for this section.

CALCULATIONS

1.0 Prepare Results Table

1.1 Obtain the chromatography data in ng/mL for the coupon extract (**CE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis. Due to the dynamic range of the data included in this analysis, several analytical methods may be used to analyze the samples. If there is a sample that reports a non-detection value and there is an analytical method with a lower detection limit, the sample should be re-run on the more sensitive method.

1.2 Calculate 'Analyte Mass Recovered' ***Rec***.

For each coupon extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Rec} \text{ (in ng)} = \mathbf{CE_E} \times \mathbf{EV} \qquad (1)$$

- **Note**: Any data that is below the analytical method's lower quantitation limit should not be reported or used in the fitting and analysis.

1.3 Calculate 'Analyte Mass Delivered' ***Del***.

For each dose confirmation sample extract, convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

1.4 Calculate the average and standard deviation of the delivered mass for all replicates of each solution. (Acceptance criteria: the relative standard deviation (std/avg) must be < 15%)

1.5 Prepare results table for each dosing concentration listing the target mass on the coupon, and delivered and recovered results.

1.6 Calculate the Extraction Efficiency (**EE**) for each sample which is calculated per Equation 3.

$$\mathbf{EE} = \boldsymbol{Rec} / \boldsymbol{Del} \qquad (3)$$

1.7 Two calibration models will be calculated. The following procedures will identify which calibration curve best represents the extraction performance.

2.0 Prepare the Independent and Relative Recovery (IRR) EE Calibration Curve

2.1 Calculate 1 / **Del** from the average calculated in step 1.4.

2.2 For each replicate sample, plot 1 / **Del** vs. **EE** (calculated in step 1.6).

- **Note**: Do not calculate an average EE for each dose solution The empirical fitting uses each **Rec** data point.

2.3 Apply a linear regression to the data.

2.4 The IRR EE calibration curve assumes the following relationship where R is a relative recovery term and I is an independent loss term. The slope obtained from step 2.3 equals -I, R equals the intercept from step 2.3

$$Rec = (Del \times R) - I \qquad (4)$$

I = -slope (of 1/Del vs. EE)

R = intercept (of 1/Del vs. EE)

2.5 Calculate the EE as a function of delivered mass for the calibration curve:

$$EE_{IRR}(Del) = R - I / Del \qquad (5)$$

2.6 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = (EE - EE_{IRR}(Del))^2 \qquad (6)$$

2.7 Calculate the sum of the square of the errors. This term is used later to select which calibration curve to use.

$$SSE_{IRR} = \Sigma\sigma^2 \qquad (7)$$

2.8 If this EE calibration curve is chosen, the EE corrected mass is calculated by

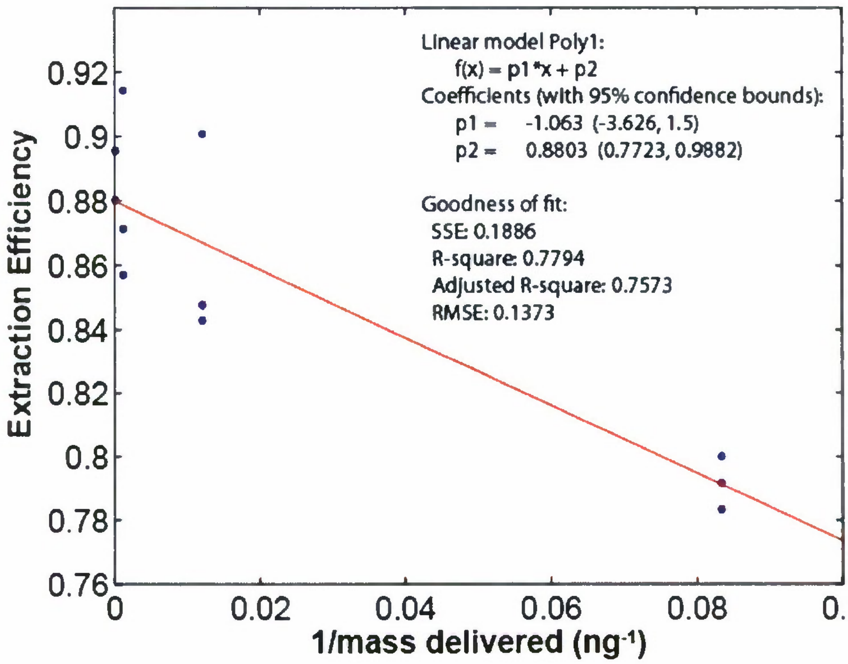
$$Mass_C = (Mass_M + I) / R \qquad (8)$$

Note: if the extracted mass (M_E) is below the limit of quantitation (LOQ), the corrected mass should be reported as below quantitation or below detection.

Sample Calculation of Step 2.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	1 / Mass Delivered (ng^{-1})	Mass Recovered (ng)	Extraction Efficiency
15	12.0 ± 1.4 [11.6%]	0.083031	9.6	0.795
			9.4	0.778
			9.5	0.785
100	82.7 ± 2.8 [3.4%]	0.012099	70.1	0.848
			69.7	0.843
			74.5	0.901
1,000	834.3 ± 16.6 [2.0%]	0.001199	726.9	0.871
			715.0	0.857
			762.7	0.914
10,000	8538.8 ± 313.3 [3.7%]	0.000117	7,646.5	0.896
			15,431.8*	1.807*
			7,515.3	0.880

*identified as statistical outlier



Calibration Curve Coefficients: I = -slope = -p1 = 1.063 (ng), R = intercept = p2 = 0.8803 (unitless)

3.0 Prepare the Power Law (PL) EE Calibration Curve

3.1 Calculate log (**Del**) from the average calculated in step 1.4.

3.2 Calculate log (**Rec**) for each replicate sample calculated in step 1.2.

3.3 For each replicate sample, plot log (**Del**) vs. log (**Rec**). Note: Do not calculate an average log (**Rec**) for each dose solution. The empirical fitting uses each individual data point.

3.4 Apply a linear regression to the data.

3.5 The PL calibration curve assumes the following relationship where the slope (m) and intercept (b)

$$\mathbf{\mathit{Rec} = 10^{b} \times Del^{m}} \qquad (9)$$

3.6 Calculate the EE as a function of delivered mass for the calibration curve:

$$\mathbf{\mathit{EE_{PL}(Del)} = (10^{b} \times Del^{m}) / Del} \qquad (10)$$

3.7 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = \mathbf{(\ EE - EE_{PL}(Del)\ )^2} \qquad (11)$$

3.8 Calculate the sum of the square of the errors

$$\mathbf{SSE_{PL} = \Sigma\sigma^2} \qquad (12)$$

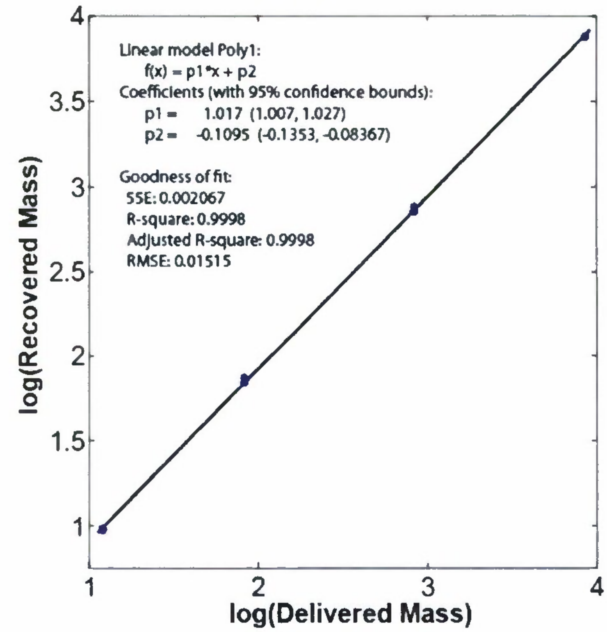
3.9 If this EE calibration curve is chosen, the EE corrected mass is calculated by

$$\mathbf{Mass_C = (Mass_M / 10^{b})^{1/m}} \qquad (13)$$

Sample Calculations of Step 3.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	Log(Del)	Mass Recovered (ng)	Log(Rec)
15	12.0 ± 1.4 [11.6%]	1.079	9.6	0.9809
			9.4	0.9718
			9.5	0.9754
100	82.7 ± 2.8 [3.4%]	1.918	70.1	1.845
			69.7	1.843
			74.5	1.871
1,000	834.3 ± 16.6 [2.0%]	2.921	726.9	2.861
			715.0	2.854
			762.7	2.882
10,000	8538.8 ± 313.3 [3.7%]	3.931	7,646.5	3.883
			15,431.8*	4.188*
			7,515.3	3.875

*identified as statistical outlier



Calibration Curve Coefficients:

m = slope = p1 = 1.017 (unitless)

b = intercept = p2 = -0.1095 (unitless)

4.0 Select the EE Calibration Curve

4.1 Compare the SSE values for each calibration curve. The calibration curve with the smaller SSE provides the better fit.

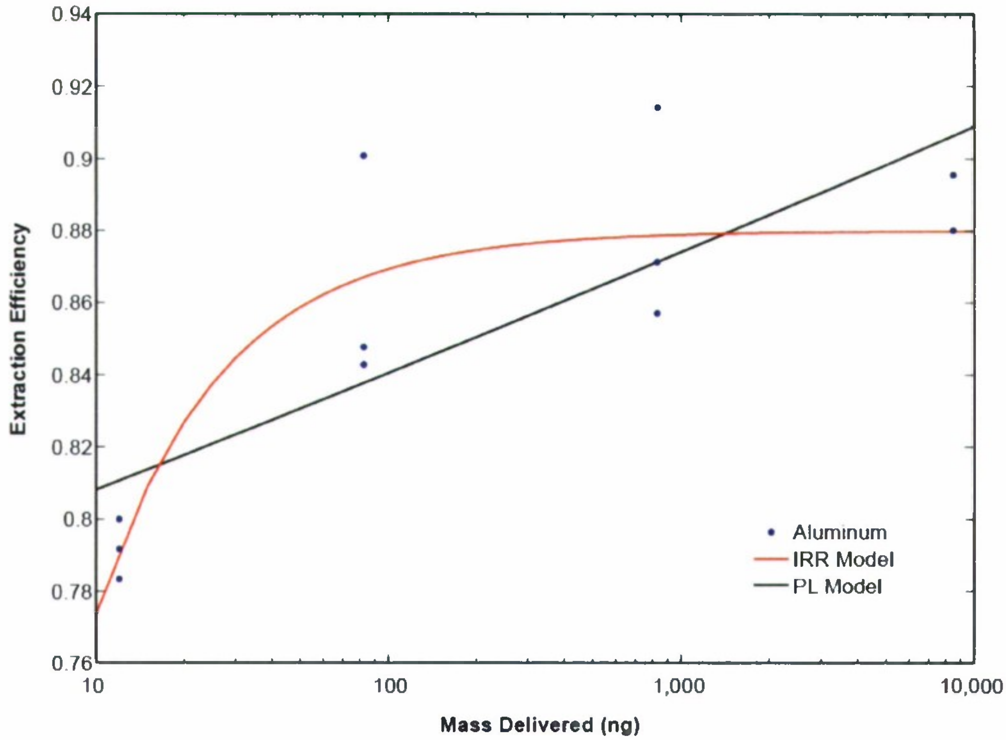
4.2 Plot **Del** vs. **EE**, and **Del** vs. $\mathbf{EE_{Model}}$ (**Del**) to visually confirm the model fits the data.

4.3 For any calculations that use extraction efficiency correction use Equation 8 if the IRR calibration curve was selected or Equation 13 if the PL calibration curve was selected.

- **Note**: The EE calibration curve has similar 'rules' of implementation as an analytical instrument calibration curve. Recovered masses applied to the EE calibration curve that are significantly outside of the tested mass values may not return accurate results.
- **Note:** Extrapolation of the EE calibration curve above the tested range must be handled with caution. Multiple EE calibration curves may be needed to test from contamination density (e.g., 1- to 10 g/m^2) extractions down to requirement (e.g., 0.05 mg/m^2) level extractions. This is especially true for the reduction in starting challenge calculations where extracted masses may be large.
- **Note**: Due to the limitations of EE testing caused by evaporation and other loss mechanisms, extrapolation to ranges below the test range qualifier will be allowed at this time.

4.4 Report which EE calibration curve was used and the coefficients used in the calibration.

Mass Del (ng)	**Data EE**	**IRR Model EE**	**IRR Residual (σ)**	**IRR σ^2**	**PL Model EE**	**PL Residual (σ)**	**PL $(\sigma)^2$**
12.0	0.7947	0.7917	0.0029	8.614E-6	0.8107	-0.0160	2.567E-4
	0.7781		-0.0136	1.842E-4		-0.0325	1.058E-3
	0.7847		-0.0070	4.857E-5		-0.0259	6.722E-4
82.7	0.8480	0.8675	-0.0195	3.789E-4	0.8377	0.0103	1.054E-4
	0.8432		-0.0243	5.893E-4		0.0055	2.974E-5
	0.9009		0.0335	1.119E-3		0.0632	3.992E-3
834.3	0.8713	0.8790	-0.0077	5.933E-5	0.8713	0.0000	1.474E-9
	0.8570		-0.0220	4.840E-4		-0.0143	2.033E-4
	0.9142		0.0352	1.238E-3		0.0429	1.843E-3
8538.8	0.8955	0.8802	0.0153	2.350E-4	0.9064	-0.0109	1.193E-4
	1.807*		N/A	N/A		N/A	N/A
	0.8801		0.0000	1.295E-9		-0.0263	6.911E-4
Goodness of Fit			**SSE**	**0.00435**		**SSE**	**0.00897**
			RMSE	**0.01988**		**RMSE**	**0.02856**
			R^2	**0.8151**		**R^2**	**0.6057**
			Corr. Coef.	**0.9028**		**Corr. Coef.**	**0.7783**



TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.

EQUIPMENT

- **Contaminant Delivery Tool**

- Tool identification including manufacturer, model number, and volume dispensing range.
    - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
    - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
    - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, or explanation of how the process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Contamination**
    - Option used (A, B or C)
        - For Option C: a description of how the contamination was performed.
    - Contamination density in g/m^2.
    - Total agent volume in microliters (μL) per coupon.
    - Agent drop volume size(s) in microliters (μL) per coupon.
    - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
    - Test location temperature and relative humidity during contamination.
    - Contaminant temperature at time of contamination.
    - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Solution Preparation**: include the number of dosing points, list of target delivered mass per test surface (e.g., coupon, contact sampler) in nanograms, corresponding list of nominal solution concentrations in nanograms per milliliter (g/mL), and a description of dosing solutions preparation.

- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the coupon test results in nanograms per coupon and "dose confirmation" sample mass in nanograms.
- **Calculation Reporting Criteria**
  - Summary data table containing the following information.
    - Data in ng/mL for the coupon extract (**CE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
    - Analyte mass recovered (***Rec***) results in ng for each test replicate for each dosing solution.
    - Delivered mass results (***Del***) in ng for each dosing solutions, average Del and RSD.
    - Extraction efficiency (**EE**) calculated for each sample.
    - Which EE calibration curve was selected - Independent and Relative Recovery (IRR) or Power Law (PL).
    - The calibration curve slope and intercept.
    - Provide the selected calibration curve.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Delivered Mass: The delivered mass for the determination of the extraction efficiency test should produce analytical results with a RPD < 15%.

- Rationale: Due to the number of tools used and steps involved in preparing the dosing solutions, the most accurate method to calculate the delivered mass is to directly measure exactly what was delivered to the sample. This enables an accurate method to determine the extraction efficiency per test sample.

EE Model: The EE calibration model selected should provide a best fit to the data. Though some materials may provide a significant distribution of results, it is recommended that an average RPD value for a model is <15%. However, it is recognized that some materials may never meet this criteria. In all cases the average RPD value should be reported.

- Note: the EE calibration model assumes all loss is due to incomplete extraction. No correction is included that accounts for 'depth' in the material that may be harder to extract.

REVISION HISTORY

March 2008: original method.

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Test Procedure 6-G: Data Calculation Method to Report Contact Hazard, Percent Neutralization, Percent Efficacy or Reduction in Starting Challenge

SUMMARY OF PROCEDURE

The objective of the decontaminant performance evaluations is to use the test data to make decisions regarding the decontaminant performance. These decisions may be based on comparisons to requirement documents or by comparison to current decontaminants. Contact Hazard, Percent Neutralization, Percent Efficacy, and Reduction in Starting Challenge are the most common performance standards reported. This section provides the detailed calculations for these performance standards.

It is recognized that there are many configurations and options that are available in these tests methods. Test execution details and measured variables determines which calculation can be used and the confidence in the calculated value. To facilitate the ability to execute these calculations with the number of permutations available in these methods requires a notation for the degree of rigor in a calculation. The terms Calculated, Approximated, and Inferred are used to indicate the level of confidence in a calculation based on the available data. Note that each calculation option indicates the specific test method used to generate the data for the calculation.

- **Calculated values** indicate the highest level of confidence and include using the optimal test configuration and measuring all pertinent values. Variable names that correspond to this level of confidence carry a subscript '$_C$'.

- **Approximated values** are used in cases where the optimal test is not executed although most pertinent data is collected. Approximated values may not account for some forms of systematic loss (e.g., evaporative loss between touches in the contact test). However, the desired value can be approximated within the specified assumptions or limitations. It must be recognized that some degree of inaccuracy may occur. Variable names that correspond to approximated values carry a subscript '$_A$'.

- **Inferred values** indicate a lower confidence calculation. Gross assumptions are made regarding some variables used in the calculation. Variable names that correspond to approximated values carry a subscript '$_I$'.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **analytical sample** - liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.

- **calculations, approximated** - a calculation is described as approximated in cases where not all variables are measured but the most pertinent data is collected. Approximated values may not account for some forms of systematic loss (e.g., evaporative loss between touches in the contact test); however, the desired value can be determined within the specified assumptions or limitations. It must be recognized that some degree of inaccuracy is inherent.

- **calculations, calculated** - a calculation is described as calculated in cases where the optimal test was executed and all pertinent values were measured. This type of calculation offers the highest level of confidence in the accuracy of the value.
- **calculations, inferred** - a calculation is described as inferred if gross assumptions are made regarding some variables used in the calculation. This type of calculation offers a lower confidence level in the accuracy of the value.
- **chemical agent** - a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **confidence interval** – a calculated range for a data set that future results are likely to fall between.
- **contact hazard** - the amount of contaminant remaining on the surface that, based on toxicological human estimates, could pose a threat to unprotected personnel touching the contaminated surface.
- **contamination set** - for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon** - test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in. diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – sample providing a mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer's specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency** - the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **hazard** - A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*

- **mass balance –** the tracking and accounting for all mass in a system, expressed in percent as total mass collected/mass delivered. A mass balance less than 1 indicates loss in the system.
- **moderate condition** – the test condition in the middle of the testing range that is the standard indoor office/laboratory condition at 19-21°C and 50-60% relative humidity.
- **neutralization -** the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption though there may be a minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **panel** – *see coupon.*
- **percent efficacy (and calculation) -** the measurement of the amount of contaminant removed from the material of interest as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **percent neutralization (and calculation) -** the measurement of the amount of contaminant reacted/neutralized as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **reduction in starting challenge (and calculation)** – the measurement of the mass of contaminant that has been removed from the material of interest. This calculation is most often employed for the evaluation of physical removal, sorbent, or pre-clean techniques. The value can be reported as calculated, approximated, or inferred.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **remaining agent -** the amount of contaminant present in/on the material of interest after the decontamination process has been conducted. This value is different from the residual agent in that no mass has been removed from the coupon by contact or vapor testing. This value cannot be used to calculate a contact- or vapor-hazard.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **residual agent** - the amount of contaminant present in/on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate -** the collected rinse from the decontamination process. The sample may include residual decontaminant, agent, or agent byproducts in water.
- **Sorptive / Porous Materials**: a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.

- **test condition -** for a specific agent–material-decon set, the combined contamination, aging, decontaminant process, environmental, and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **touch -** a contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration, and skin condition (wet versus dry). For the coupon test, the contact area is nominally the coupon area. The pressure is 0.7 to 1.0 psi (0.05 to 0.07 kg/cm^2) pressure which is equivalent to a 1 kg contact mass that is cylindrical with a 2 in. diameter. The contact time is typically 15 min.
- **uncertainty of measurement** – a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

REFERENCED DOCUMENTS

- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

PERCENT EFFICACY CALCULATION

Percent Efficacy is defined as the total measured agent from the material of interest following a decontamination treatment process. The direct calculation (Options A and B) requires the mass from the dose confirmation sample for delivered mass and the extraction results corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown in Option C.

$$\textbf{Efficacy}\ (\%) = (\ 1 - (\textbf{recovered agent}\ /\ \textbf{delivered agent})\ )\ \text{x}\ 100\% \qquad (1)$$

<u>**OPTION A – Calculated Efficacy for Procedure 6-E Remaining Agent**</u>: This is the preferred method from the calculation of percent efficacy as the remaining agent measurement is performed directly after the decontamination treatment. This direct calculation requires the mass from the dose confirmation sample for delivered mass and the remaining agent mass corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown for Option C. This calculation can be applied to the baseline positive control test results to calculate percent efficacy.

$$\mathbf{EFF_{C\text{-}RA}}\ (\%) = (\ 1 - (\mathbf{RA_C}\ /\ \mathbf{DC_M})\ )\ \text{x}\ 100\% \qquad (2)$$

where

$\mathbf{EFF_{C\text{-}RA}}$ = efficacy calculated from remaining agent (%)

$\mathbf{RA_C}$ = remaining agent mass corrected for extraction efficiency (ng)

$\mathbf{DC_M}$ = dose confirmation mass (ng)

<u>**OPTION B – Calculated Efficacy for Procedure 6-A Contact Test**</u>: Percent efficacy can be calculated using the contact sampler results (note definition as total measured agent, evaporative loss between touches is not included). The potential for lost agent is greater with more test actions (i.e., contact samplers, additional dwell times) and this effect on the final

reported result should be considered during test design. This direct calculation requires the mass from the dose confirmation sample for delivered mass and the contact and residual agent masses corrected for extraction efficiency. If any value is not available, then an inferred percent efficacy can be calculated as shown for Option C. This calculation can be applied to the baseline positive control test results to calculate percent efficacy.

$$\mathbf{EFF_{C\text{-}CT}}\ (\%) = (1 - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_C}) / \mathbf{DC_M})) \times 100\% \qquad (3)$$

where

$\mathbf{EFF_{C\text{-}CT}}$ = efficacy calculated from contact test results (%),
$\mathbf{CS_C}$ = contact sampler mass corrected for extraction efficiency (ng)
$\Sigma(\mathbf{CS_C})_n$ = sum of all contact tests (ng)
$\mathbf{RE_C}$ = residual agent mass corrected for extraction efficiency (ng)
$\mathbf{DC_M}$ = dose confirmation mass (ng)

<u>OPTION C – Inferred Efficacy Calculation</u>: The inferred calculation is used for tests missing the dose confirmation sample for delivered mass and/or if the agent mass (e.g., contact, residual and/or remaining) is **NOT** corrected for extraction efficiency. This calculation can be applied to the baseline positive control test results to calculate percent efficacy. Several options of what this calculation may look like are shown in Equations 4 through 8. Note, not all variations are shown. The specific version of the equation used must be documented in the final report.

$$\mathbf{EFF_{I\text{-}RA}}\ (\%) = (1 - (\mathbf{RA_M} / \mathbf{DC_M})) \times 100\% \qquad (4)$$

$$\mathbf{EFF_{I\text{-}RA}}\ (\%) = (1 - (\mathbf{RA_C} / \mathbf{SC_M})) \times 100\% \qquad (5)$$

$$\mathbf{EFF_{I\text{-}RA}}\ (\%) = (1 - (\mathbf{RA_M} / \mathbf{SC_M})) \times 100\% \qquad (6)$$

$$\mathbf{EFF_{I\text{-}CT}}\ (\%) = (1 - ((\Sigma(\mathbf{CS_M})_n + \mathbf{RE_C}) / \mathbf{DC_M})) \times 100\% \qquad (6)$$

$$\mathbf{EFF_{I\text{-}CT}}\ (\%) = (1 - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_M}) / \mathbf{DC_M})) \times 100\% \qquad (7)$$

$$\mathbf{EFF_{I\text{-}CT}}\ (\%) = (1 - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_C}) / \mathbf{SC_M})) \times 100\% \qquad (8)$$

where

$\mathbf{CS_C}$ = contact sampler mass corrected for extraction efficiency (EE) (ng)
$\mathbf{CS_M}$ = contact sampler mass – not EE corrected (ng)
$\Sigma(\mathbf{CS_X})_n$ = sum of all contact tests
$\mathbf{DC_M}$ = dose confirmation mass (ng)

$EFF_{I\text{-}RA}$ = inferred efficacy calculated from remaining agent test results (%)
$EFF_{I\text{-}CT}$ = inferred efficacy calculated from contact test results (%)
RA_C = remaining agent mass corrected for extraction efficiency (ng)
RA_M = remaining agent mass – not EE corrected (ng)
RE_C = residual agent mass corrected for extraction efficiency (ng)
RE_M = residual agent mass – not EE corrected (ng)
SC_M = starting challenge mass multiplied by the coupon surface area (ng)

REDUCTION IN STARTING CHALLENGE CALCULATION

Reduction in Starting Challenge is defined as the difference in contamination density between the starting challenge delivered and the agent recovered from the material of interest. The test area is the original area identified for the contamination. For the 2 in. diameter circular coupons, it is the coupon surface area (0.00202 m^2). For larger panels, it is the area marked off via grease pencil (or equivalent) for contamination application. This area should not be confused with the contaminated surface area which is the fraction of the test area covered with agent. The direct calculation (Option A) requires the mass from the dose confirmation sample for delivered mass and the remaining agent extraction results corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown in Option C. A variation of the calculation using contact test data is provided as Option B. Note that reducing a 10 g/m^2 starting challenge to a 1 g/m^2 contamination density would result in a 9 g/m^2 starting challenge reduction.

$$\textbf{Starting Challenge Reduction}\ (g/m^2) = \frac{\textbf{(delivered agent – recovered agent)}}{\textbf{test area}} \qquad (9)$$

<u>**OPTION A – Calculated Reduction in Starting Challenge for Procedure 6-E Remaining Agent**</u>: This is the preferred method for the reduction in starting challenge calculation as the remaining agent measurement is performed directly after the decontamination treatment. This direct calculation requires the mass from the dose confirmation sample for delivered mass and the remaining agent mass corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown for Option C. This calculation can be applied to the baseline positive control test results to calculate reduction in starting challenge.

$$\mathbf{RSC_{C\text{-}RA}}\ (g/m^2) = (\mathbf{DC_M} - \mathbf{RA_C}) \ / \ (\mathbf{CA} \times 10^9) \qquad (10)$$

where
$RSC_{C\text{-}RA}$ = reduction in starting challenge calculated from remaining agent (g/m^2)
RA_C = remaining agent mass corrected for extraction efficiency (ng)
DC_M = dose confirmation mass (ng)
CA = test area (m^2)

<u>OPTION B – Approximated Reduction in Starting Challenge for Procedure 6-A Contact Test</u>: This is an approximated method for the reduction in starting challenge calculation using contact test results. This direct calculation requires the mass from the dose confirmation sample for delivered mass and the remaining agent mass corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown for Option C. This calculation can be applied to the baseline positive control test results to calculate reduction in starting challenge.

$$\mathbf{RSC_{A\text{-}CT}}\ (g/m^2) = (\mathbf{DC_M} - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_C}))\ /\ (\mathbf{CA} \times 10^9) \qquad (10)$$

where

$\mathbf{RSC_{A\text{-}CT}}$	= approximated reduction in starting challenge calculated from contact test results (g/m^2)
$\mathbf{DC_M}$	= dose confirmation mass (ng)
$\mathbf{CS_C}$	= contact sampler mass corrected for extraction efficiency (ng)
$\Sigma(\mathbf{CS_C})_n$	= sum of all contact tests
$\mathbf{RE_C}$	= residual agent mass corrected for extraction efficiency (ng)
$\mathbf{CA}$	= test area (m^2)

<u>OPTION C – Inferred Reduction in Starting Challenge Calculation</u>: The inferred calculation is used for tests missing the dose confirmation sample for delivered mass and/or if the agent mass (e.g., contact, residual and/or remaining) is **NOT** corrected for extraction efficiency. This calculation can be applied to the baseline positive control test results to calculate percent efficacy. Several options of what this calculation may look like are shown in Equations 11 through 16. Note, not all variations are shown. The specific version of the equation used must be documented in the final report.

$$\mathbf{RSC_{I\text{-}RA}}\ (g/m^2) = (\mathbf{DC_M} - \mathbf{RA_M}\ )\ /\ (\mathbf{CA} \times 10^9) \qquad (11)$$

$$\mathbf{RSC_{I\text{-}RA}}\ (g/m^2) = (\mathbf{SC_M} - \mathbf{RA_C}\ )\ /\ (\mathbf{CA} \times 10^9) \qquad (12)$$

$$\mathbf{RSC_{I\text{-}RA}}\ (g/m^2) = (\mathbf{SC_M} - \mathbf{RA_M}\ )\ /\ (\mathbf{CA} \times 10^9) \qquad (13)$$

$$\mathbf{RSC_{I\text{-}CT}}\ (g/m^2) = (\mathbf{DC_M} - ((\Sigma(\mathbf{CS_M}))_n + \mathbf{RE_C}))\ /\ (\mathbf{CA} \times 10^9) \qquad (14)$$

$$\mathbf{RSC_{I\text{-}CT}}\ (g/m^2) = (\mathbf{DC_M} - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_M}))\ /\ (\mathbf{CA} \times 10^9) \qquad (15)$$

$$\mathbf{RSC_{I\text{-}CT}}\ (g/m^2) = (\mathbf{SC_M} - ((\Sigma(\mathbf{CS_C})_n + \mathbf{RE_C}))\ /\ (\mathbf{CA} \times 10^9) \qquad (16)$$

where

CS_C	= contact sampler mass corrected for extraction efficiency (ng)
CS_M	= contact sampler mass (ng)
$\Sigma(CS_X)_n$	= sum of all contact tests
DC_M	= dose confirmation mass (ng)
$RSC_{I\text{-}RA}$	= inferred reduction in starting challenge calculated from remaining agent test results (%)
$RSC_{I\text{-}CT}$	= inferred reduction in starting challenge calculated from contact test results (%)
RA_C	= remaining agent mass corrected for extraction efficiency (ng)
RA_M	= remaining agent mass (ng)
RE_C	= residual agent mass corrected for extraction efficiency (ng)
RE_M	= residual agent mass (ng)
SC_M	= starting challenge mass divided by the coupon surface area (ng)

PERCENT NEUTRALIZATION CALCULATION

Percent Neutralization is the destruction in the amount of the agent as part of the decontamination process accounting for any agent physically removed as part of the decontamination process. The specific objective is to calculate the agent destroyed by the decontaminant. Option A is the rigorous calculation for calculating percent neutralization from remaining agent test results. This procedure requires the baseline positive control results to account for systematic losses such as evaporation, degradation, reaction with materials, and coupon handling. The direct calculation also requires the mass from the dose confirmation sample for delivered mass and the remaining agent extraction results corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown in Option C. Option A is preferred when high data confidence is required. Option C provides guidance for calculating an inferred percent neutralization. The Option C calculated result has the potential of lower certainty due to the additional test and coupon handling steps. A comparison of the Procedure 6-E and Procedure 6-D baseline tests for the same operation can provide guidance to test and handling losses. The contaminated area relative surface coverage should be similar for the test data and baseline data being compared for accurate calculation of percent neutralization.

$$\textbf{Baseline Loss}\text{ (ng)} = \textbf{baseline delivered agent} - \textbf{total baseline recovered agent} \qquad (17)$$

$$\textbf{Adjusted Delivered Agent}\text{ (ng)} = \textbf{Delivered Agent} - \textbf{Baseline Loss} \qquad (18)$$

$$\textbf{Neutralization}\text{ (\%)} = \left(1 - \left(\frac{\textbf{total recovered agent}}{\textbf{adjusted delivered agent}}\right)\right) \times 100\% \qquad (19)$$

<u>**OPTION A – Calculated Percent Neutralization for Procedure 6-E Remaining Agent**</u>: This is the preferred method for the percent neutralization calculation as the remaining agent measurement is performed directly after the decontamination treatment. This calculation also requires the baseline positive control results to correct the amount delivered to account for

systematic losses. This method assumes that the baseline loss (e.g., evaporation) is constant. Changes in temperature or airflow conditions could significantly affect the baseline loss value. Thus, the positive control sample and test temperatures must be similar. Further, because the baseline loss incorporates evaporative loss, the value is specific to aging and decon residence times (i.e., agent may continue evaporating during the decon residence time, especially for vaporous decontaminants). This direct calculation requires the mass from the dose confirmation sample for delivered mass, the remaining agent mass, and recovered agent from rinse water all corrected for extraction efficiency. If either value is not available, then an inferred percent efficacy can be calculated as shown for Option C.

The baseline test results are used to calculate baseline delivered agent ($\mathbf{DA_B}$). Since this test uses the extraction efficiency corrected values, the delivered agent is represented as $\mathbf{DA_{C\text{-}B}}$ for extraction corrected.

$$\mathbf{BL_{C\text{-}B}}\ (\mathrm{ng}) = \mathbf{DC_{M\text{-}B}} - (\mathbf{RA_{C\text{-}B}} + \mathbf{RI_{C\text{-}B}}) \qquad (20)$$

where

- $\mathbf{BL_{C\text{-}B}}$ = baseline loss mass as determined from the baseline positive control test accounting for systematic loss (ng)
- $\mathbf{DC_{M\text{-}B}}$ = dose confirmation mass (ng) for baseline test
- $\mathbf{RA_{C\text{-}B}}$ = remaining agent mass corrected for extraction efficiency (ng), for baseline test
- $\mathbf{RI_{C\text{-}B}}$ = recovered agent from rinse water corrected for extraction efficiency (ng), for baseline test

The percent neutralization is calculated using the remaining agent test results and the delivered agent as determined from the baseline positive control test accounting for systematic loss.

$$\mathbf{NEU_{C\text{-}RA}}\ (\%) = (1 - ((\mathbf{RA_C} + \mathbf{RI_C}) / (\mathbf{DC_M} - \mathbf{BL_{C\text{-}B}}))) \times 100\% \qquad (21)$$

where

- $\mathbf{NEU_{C\text{-}RA}}$ = percent neutralization calculated from remaining agent results (%)
- $\mathbf{BL_{C\text{-}B}}$ = Baseline loss mass calculated in Equation 20 (ng)
- $\mathbf{DC_M}$ = dose conformation mass (ng)
- $\mathbf{RA_C}$ = remaining agent mass corrected for extraction efficiency (ng)
- $\mathbf{RI_C}$ = recovered agent from rinse water corrected for extraction efficiency (ng). Note if pre-rinse is used: this value must be the sum of both pre-rinse and post-rinse.

<u>OPTION B – Approximated Percent Neutralization for Procedure 6-A Contact Test</u>: This is an approximated method for the percent neutralization calculation using contact test results. This approximation requires the mass from the dose confirmation sample for delivered mass, the contact, residual, and recovered agent from rinse water masses all be corrected for extraction efficiency. If any value is not available, then an inferred percent efficacy can be calculated as shown for Option C.

The baseline test results are used to calculate baseline delivered agent (**DA_B**). Since this test uses the extraction efficiency corrected values, the delivered agent is represented as **$DA_{C\text{-}B}$** for extraction corrected.

$$BL_{A\text{-}B}\,(ng) = DC_{M\text{-}B} - (\Sigma(CS_{C\text{-}B})_n + RE_{C\text{-}B} + RI_{C\text{-}B}) \qquad (22)$$

where

$BL_{A\text{-}B}$	=	baseline loss mass as determined from the baseline positive control test accounting for systematic loss (ng)
$DC_{M\text{-}B}$	=	dose confirmation mass (ng) for baseline test
$CS_{C\text{-}B}$	=	contact sampler mass corrected for extraction efficiency (ng), for baseline test
Σ(**$CS_{C\text{-}B}$**)$_n$	=	sum of all contact tests for baseline test
$RE_{C\text{-}B}$	=	residual agent mass corrected for extraction efficiency (ng)
$RI_{C\text{-}B}$	=	recovered agent from rinse water corrected for extraction efficiency (ng), for baseline test. Note if pre-rinse is used: this value must be the sum of both pre-rinse and post-rinse.

The percent neutralization is calculated using the remaining agent test results and the delivered agent as determined from the baseline positive control test accounting for systematic loss.

$$NEU_{C\text{-}CT}\,(\%) = (1 - ((\Sigma(CS_C)_n + RE_C + RI_C\,)\,/\,(DC_M - BL_{C\text{-}B}\,)\,)\,) \times 100\% (23)$$

where

$NEU_{C\text{-}CT}$	=	percent neutralization calculated from remaining agent results (%)
$DA_{C\text{-}B}$	=	delivered agent as determined from the baseline positive control test accounting for systematic loss (ng)
DC_M	=	dose conformation mass (ng)
CS_C	=	contact sampler mass corrected for extraction efficiency (ng)
Σ(**CS_C**)$_n$	=	sum of all contact tests
RE_C	=	residual agent mass corrected for extraction efficiency (ng)
RI_C	=	recovered agent from rinse water corrected for extraction efficiency (ng). Note if pre-rinse is used: this value must be the sum of both pre-rinse and post-rinse.

<u>OPTION C – Inferred Percent Neutralization Calculation</u>: The inferred calculation is used for tests missing the dose confirmation sample for delivered mass and/or if the agent mass (e.g., contact, residual, and/or remaining) is **NOT** corrected for extraction efficiency. Calculations 24 and 25 are shown with what substitutions can be made to calculate inferred agent if corrected masses are not available. The specific version of the equation used must be documented in the

final report. The inferred value likely overestimates neutralization as most loss terms will be calculated as neutralization.

$$BL_B \text{ (ng)} = SC_M - RA_{M\text{-}B} - RI_{M\text{-}B} \tag{24}$$

$$NEU_{I\text{-}RA} \text{ (\%)} = (1 - ((RA_C + RI_C) / (SC_M - BL_B))) \times 100\% \tag{25}$$

where

BL_B	=	baseline loss mass as determined from the baseline positive control test not accounting for systematic loss (ng)
SC_M	=	starting challenge mass multiplied by the coupon surface area (ng)
$RA_{M\text{-}B}$	=	remaining agent mass (ng), for baseline test
$RI_{M\text{-}B}$	=	recovered agent from rinse water (ng), for baseline test. Note if pre-rinse is used: this value must be the sum of both pre-rinse and post-rinse.
$NEU_{I\text{-}RA}$	=	inferred percent neutralization calculated from remaining agent results (%) not accounting for systematic loss or extraction efficiency
RA_C	=	remaining agent mass corrected for extraction efficiency (ng)
RI_C	=	recovered agent from rinse water corrected for extraction efficiency (ng). Note if pre-rinse is used: this value must be the sum of both pre-rinse and post-rinse.

CONTACT HAZARD CALCULATION

Contact Hazard Requirement Comparison Calculation is the conversion of the Procedure 6-A contact test results into a value that can be compared to a requirement document. This calculation generates a value in requirement units for guidance purposes. The requirements lack sufficient information for a rigorous calculation for a direct comparison. The test director and sponsor should ensure that the contact test conducted aligns with the expectations for data use. The calculation shown is for Procedure 6-A Option A that uses two touches of 15 minutes each within 60 minutes of the end of the decontamination treatment.

Limitations of the calculation:

- The contact hazard is only measured and known for the test time (60 minutes after decontamination).
- The measurement of residual agent may provide guidance if agent is present in the material after the touch events that may pose a future hazard.
- The CS_C mass represents the mass transferred to the contact sampler. The correlation of the contact sampler uptake to skin is not addressed here. (see Reutter 06, Appendix D).
- The requirements do not specify touch duration or touch area. This reported value corresponds to the mass of agent absorbed by the contact sampler for two touches each lasting 15 minutes, divided by the area of the test coupon, reported in the same units as the requirements.

$$CC_{C\text{-}CT}\ (mg/m^2) = (CS_{C1} + CS_{C2})\ /\ (CA \times 10^6) \quad (26)$$

where

$CC_{C\text{-}CT}$	=	calculated contact hazard comparison value from contact test results (mg/m^2)
DC_M	=	dose confirmation mass (ng)
CS_{C1}	=	contact sampler mass corrected for extraction efficiency for touch #1 (ng)
CS_{C2}	=	contact sampler mass corrected for extraction efficiency for touch #2 (ng)
CA	=	test coupon area (m^2)

REPORTING

The calculation results should include sufficient information that the degree of calculation and context are clear. The reporting information includes:

- Name of calculation(s) performed (e.g., Contact Hazard, Percent Neutralization, Percent Efficacy, and Reduction in Starting Challenge).
- Provide the equations used. It is recommended that these are documented as part of the experimental section and referred to in test result text.
- Calculated result using nomenclature defined in Procedure 6-G for calculated, approximated, or inferred.
- Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

REVISION HISTORY

March 2008: original method.

Test Procedure 6-H: Chromatographic Analysis Guidance

SUMMARY

Program CA06DEC407 was a DTRA funded effort designed to address the challenges associated with quantifying low-level residual agent to support decontaminant contact- and vapor-test evaluations. The program had three main objectives.

- The primary program objective was to develop improved analytical methods to enable the confident detection of low-level of chemical agents VX, HD and GD at published requirement levels for testing using the 2-in. diameter circular coupons.
    - The lowest requirements at the time of this program used to establish the required detection limits were the Joint Platform Interior Decontamination (JPID) program 2003 and the Joint Service Sensitive Equipment Decontamination (JSSED) program 2005 requirement documents.
- The secondary program objective was to establish methods for the detection of common agent byproducts that could form during decontaminant testing.
- The tertiary program objective was to make the new methods available to establish uniformity in test procedures across testing locations.

The methods were written for analysis using mass selective detectors. Mass selective detectors were selected to increase confidence that the reported data was for the analyte of interest and not an interferent, product or other analyte. Other detection methods can be used, though mass selective detectors are recommended. The methods are formally documented in Appendix C. Each method is documented as an individual method. The methods are constructed using standardized fields with all pertinent information. The 'Analyte Concentration Range' section provides an overview of the method target, the calibration range, calibration curve fitting model and weighting, limit of detection (LOD), limit of quantitation (LOQ), solvent and quantitation ion(s). The methods are identified as quantitative or qualitative. The secondary program objective was byproduct identification. The byproduct methods as presented are qualitative. All qualitative methods in this document can be quantitative if a set of calibration standards of the byproduct are prepared and analyzed. The LOD and LOQ are calculated based on the laboratory evaluation of the final method. Each laboratory should recalculate these values based on their method performance. LOD and LOQ are a function of instrument sensitivity which can decay over time/use. Instrument sensitivity can often be restored by regular scheduled maintenance, thus illustrating the need for a regular maintenance schedule. It is anticipated that a laboratory can achieve the appearance of a better LOD and LOQ, especially for new equipment or following instrument maintenance. These values should be calculated over a period of time to determine the laboratory performance. The "Apparatus" section details the analytical equipment and standard preparation tools. The "Method Parameters" section provides the complete listing of instrumentation settings for the method.

The methods are established on the instrumentation software and configurations described in this document. These parameters may be used on similar or other GC/MS and/or LC/MS platforms and are comprehensive enough to serve as a guide for establishing low-level methods. Methods transferred to instruments set-up as described should obtain similar results; however, parameters applied to instrumentation different than described may not produce the same results. Method check-out must be performed, to include analyzing solvent blanks, chemical agent standards and by-product standards to verify instrument specific performance and method optimization. Table 6H-1 contains a summary listing of the agent, by-product, concentration range and corresponding analytical method for analysis. The method limits of detection and quantitation determined through the method development are also document.

Each lab using these methods is encouraged to determine their laboratory performance for the methods used to support decontaminant performance evaluations.

Table 6H-1. Method listing for liquid extract samples.

Compound	Range of Standards	Method Name	Appendix Method
VX	0.05 – 10 ng/mL	LCE VX_ULL.dam	A
EA2192	0.05 – 10 ng/mL	LCE VX_ULL.dam	A
VX	10 – 750 ng/mL	LCE VX_LL.dam	B
EA2192	10 – 750 ng/mL	LCE VX_LL.dam	B
EMPA	5.0 – 500 ng/mL	LCE EMPA.dam	C
VX	500 – 2000 ng/mL	GCE VX_DEANS.M	E
HD	2 – 25 ng/mL	GCE HD_DEANS.M LL	H
HD	25 – 2000 ng/mL	GCE HD_DEANS.M HL	H
H-Sulfone	10 – 2000 ng/mL	GCE H-Sulfone_DEANS.M	N
TDG	25,000 – 100,000 ng/mL	GCE TDG_DEANS.M	L
H-Sulfoxide	10 – 500 ng/mL	LCE H-Sulfoxide.dam	M
GD	2.5 – 50 ng/mL	GCE GD_DEANS.M ULL	K
GD	50 – 2000 ng/mL	GCE GD_DEANS.M LL	K
GD-acid	5,000 – 500,000 ng/mL	GCE GD-ACID_DEANS.M	O

REFERENCED DOCUMENTS

- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document," and references therein.
- DTIC published technical report by T. Lalain, et. al., titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations," and references therein.
- Kiser, M. M.; Dolan, J. W., Selecting the Best Curve Fit. LC GC *Europe* 2004, 17, (3), 138-143.
- ARMY *Environmental Quality: Guidance for Evaluating Performance-Based Chemical Data*; EM 200-1-10; US ARMY Corps of Engineers: 2005.
- FDA Guidance for Industry: Bioanalytical Method Validation. http://www.fda.gov/cder/guidance/index.htm (December, 2007).

GUIDANCE

The methods and this guidance section are written for an audience skilled in chromatographic analysis. This section provides guidance based on the low-level development learnings that could affect the accuracy and data quality for decontaminant performance evaluations.

Calibration Curve Fitting: One of the many important factors in quantitative analysis is the accuracy of a calibration curve. The accuracy of the reported result is dependent on the accuracy of all procedures used in the preparation of a calibration curve from making the standards to the regression of the detector response to generate a 'calibration curve.' Verification that an accurate calibration curve has been acquired requires a statistical analysis of the results. A single universal indicator/value for detecting the 'right' curve or a good calibration has been an elusive goal; the evaluation of a calibration model requires several types of analysis to confirm an acceptable calibration. While the evaluation of a correlation coefficient (r) or coefficient of determination (r^2) is a common method to evaluate a calibration curve, it is not a full description of the system. The coefficient of determination (r^2) indicates a correlation between the data and the calibration; it does not indicate accuracy or lack of fit. To demonstrate how r^2 can be misleading and provide guidance on how to evaluate a calibration model, a demonstration using VX on a LC/MS/MS system is illustrated. The following demonstration illustrates the impact of weighting; the same principles apply to the selection of the calibration model (i.e., which equation to use for the calibration curve).

Figure 6H-1 shows the data collected from a LC/MS/MS for a set of VX standards. Using Matlab, a linear regression was applied to the data and calibration coefficients were determined. The r^2 value for this fit was 0.9993, indicating excellent correlation. There are several misleading aspects to Figure 6H-1. It is tempting (and often assumed) that the very high r^2 value implies a good fit and that the calibration curve is acceptable for use. Visual inspection of the curve indicates that the line goes through all of the data points, also implying a good fit. However, the dynamic range of the detector response and concentration each cover three orders of magnitude. As a result of the large dynamic range and the use of a linear graph scale the lowest four standards represent 40% of the data and are graphed on only 0.01% of the graph area. As a result, the low concentration standards cannot be visually resolved for inspection.

VX Conc. (ng/mL)	Detector Response (counts)
0.101	6,320
0.203	11,900
0.496	26,800
0.993	52,300
2.480	125,000
5.060	254,000
10.125	549,000
25.313	1,250,000
49.630	2,600,000
99.267	4,920,000

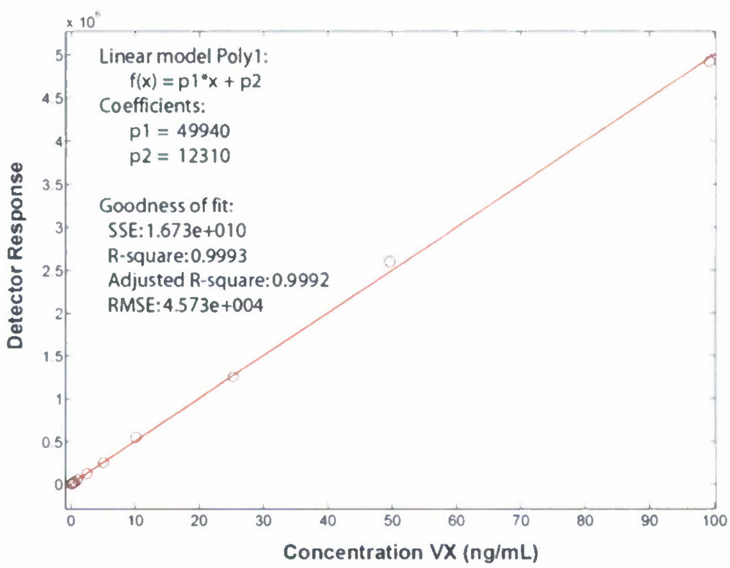

Figure 6H-1. VX calibration curve with linear plot.

To compensate for the compression of the x- and y-axes when using a linear scale, the same data should be plotted on a log-log scale, as seen in Figure 6H-2. From this graph it is immediately apparent that the calibration model does not pass through the low concentration

standards. The deviation of the calibration model from the standards would impart a substantial bias to the results. Keep in mind the r^2 value for this fit was 0.9993, even with a poor fit at low concentrations. The compression of the linear scale graph did not enable this deviation to be readily observed.

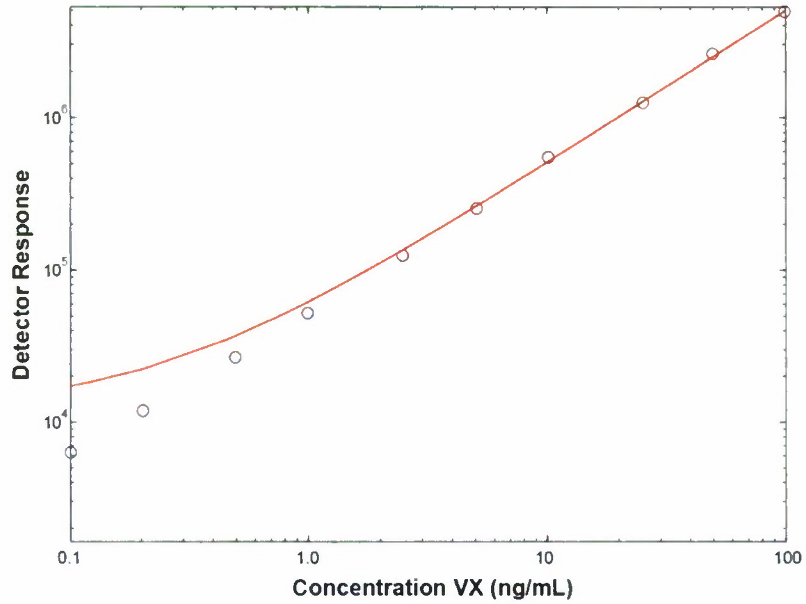

Figure 6H-2. Log-log scale VX calibration model.

This leads to the question of how much error is present in the calibration. There are several methods that can be applied to assess the error in the calibration model including residual analysis which is presented in the goodness of fit parameters in Figure 6H-1 as the sum of the square of the errors (SSE) and root mean square error (RMSE). The SSE and RMSE values are calculated from the difference in the detector response to the calibration model response (y value) at the tested concentrations. For both SSE and RMSE a smaller value represents a better fit, however these values are not normalized and a good fit for one instrument could produce SSE values orders of magnitude different than another instrument. RMSE and SSE are excellent indicators for comparison of different models for the same data, where the smaller value indicates the better fit.

Another method to analyze error in the calibration model is to calculate the concentration (x) of a standard based on its detector response (y) from the calibration model and compare it to the known concentration. For example, applying the calibration model to the response (549,000) of the 10.125 ng/mL results in a concentration of

$$x = \frac{y-b}{m} = \frac{549000-12310}{49940} = 10.747 \text{ ng/mL} .$$

The error of the calibration model to the known concentration (C_{known}) can be calculated using two methods, relative percent deviation RPD and recovery. The RPD can be calculated as

$$RPD = \frac{C_{model}-C_{known}}{\left(\frac{C_{model}+C_{known}}{2}\right)} \times 100\% = \frac{10.747-10.125}{\left(\frac{10.747+10.125}{2}\right)} \times 100\% = 5.96\% .$$

A RPD closer to zero represents a better fit. Because this form of RPD does not use an absolute value in the numerator, the value indicates a negative or positive bias to the value. The above value indicates a slight (5.96%) positive bias (i.e., the model returns a higher concentration than the 'known' value). The second method uses the concept of recovery as defined by (FDA 2007)

$$\text{recovery} = \frac{C_{\text{model}}}{C_{\text{Known}}} \times 100\% = \frac{10.747}{10.125} \times 100\% = 106.1\% .$$

A recovery closer to 100% indicates a better fit. Similar to the RPD, the recovery value of 106.2% indicates that the model introduces a slight positive bias to the data. Both the recovery and RPD methods supply a normalized result where common acceptance criteria can be established. Standard good analytical practices use CCVs to ensure that instrument calibration is maintained throughout the run sequence; pass/fail criteria for the CCVs on a mass spectrometer is usually ±30% RPD. Because RPD is already being calculated for the CCVs, it is recommended here that RPD be used to characterize the error in the calibration model. It is recommended that the acceptance criteria for a calibration curve should be equal to or more stringent than the criteria for CCVs. Other agencies, such as the FDA, have recommended that all standards above the LOQ should have a RPD less than ±15%, and that standards at the LOQ should have an RPD less than ±20% RPD.(FDA 2007)

To continue the example of the VX calibration curve, Table 6H-2 illustrates the concentration calculated from the calibration model and the RPD for each standard. The RPD values for the lower concentrations clearly indicate a poor fit, in addition to the calibration model returning negative values at lower concentrations. If this calibration model had been accepted for use based on the r^2 value alone, low concentration samples could have underestimated the real hazard by a factor of 2 or more (assuming negative values were rejected). Ideally, if the appropriate calibration model was selected the RPD values should be equally (and randomly) distributed about zero. A trend or curvature in a plot of concentration vs. RPD indicates that a different calibration model or weighting should be used.

Table 6H-2. RPD values for a linear regression with VX standards on LCE.

VX Concentration (ng/mL)	Detector Response (counts)	Calc. Conc. (ng/mL)	RPD (%)
0.101	6320	-0.120	-2332.61%
0.203	11900	-0.008	-216.86%
0.496	26800	0.290	-52.37%
0.993	52300	0.801	-21.43%
2.480	125000	2.257	-9.44%
5.060	254000	4.840	-4.45%
10.125	549000	10.747	5.96%
25.313	1250000	24.784	-2.11%
49.630	2600000	51.816	4.31%
99.267	4920000	98.272	-1.01%

The RPD analysis has indicated that a direct linear regression on the data does not produce an acceptable calibration model, the next question leads to how to identify the appropriate calibration model. In this case, the reason for the poor fit in the direct linear regression is related to the heteroscedasticity of the data. (Kiser 2004) Heteroscedastic data are characterized by a system where the absolute error (e.g., standard deviation) of a response varies with the abscissa (e.g., concentration). For heteroscedastic data, the standard deviation of the detector response for multiple analyses of a low level standard is smaller than that for a high level standard. However, the relative standard deviations (RSD), the standard deviation divided by the mean, for heteroscedastic data are typically consistent across concentrations. This is typical for most chromatographic detectors. If the data are homoscedastic, the standard deviations of the responses are independent of concentration.

Weighting of a calibration curve is appropriate if the data are heteroscedastic. Weighting is needed because the higher concentration standards are dominating the regression analysis. By applying a weighting to lower concentration standards, such as a 1/concentration weighting, the contributions of the low concentration standards can be balanced with the higher concentration standards. Table 6H-3 shows the impact of weighting on the calculated concentration and RPD for four weightings. The $1/x^n$ notation corresponds to $1/\text{concentration}^n$ for this data, n=0 corresponds to no weighting, n=0.5 corresponds to 1/square root(x). An additional term is introduced in the goodness of fit parameters, which is the sum of the absolute value of the RPD for all standards. Much like SSE, this value is not normalized, and a smaller number indicates a better fit. The sum of the absolute value of the RPD is a gauge for the performance of the fit across all data points. It is not optimal to select a calibration model based on the RPD for a particular standard, but rather the model that best represents all standards. For example, if the weighting was selected by only the lowest level standard (0.1 ng/mL) the $1/x^2$ weighting provides the lower RPD, however for the 0.2 ng/mL standard the 1/x weighting provides smaller RPD. It is better to look at the RPD of the system which is best represented by the sum of the absolute value of the RPDs. Note that the r^2 value changes by only 0.04% (and that the more accurate fits have the lower r^2 values) from the $1/x^2$ weighting to $1/x^0$ weighting, yet the accuracy of the calibration model is significantly different (Figure 6H-2).

Table 6H-3. Regression of the VX calibration using a linear calibration model with different weighting.

VX Known Conc. (ng/mL)	Detector Response (counts)	$1/x^0$ (none) Calc. Conc. (ng/mL) / [RPD %]	$1/x^{0.5}$ Calc. Conc. (ng/mL) / [RPD %]	$1/x^1$ Calc. Conc. (ng/mL) / [RPD %]	$1/x^2$ Calc. Conc. (ng/mL) / [RPD %]
0.101	6320	-0.120 / [2332]	0.065 / [-43.70]	0.094 / [-6.95]	0.099 / [-1.54]
0.203	11900	-0.008 / [-217]	0.176 / [-14.35]	0.205 / [0.84]	0.209 / [2.74]
0.496	26800	0.290 / [-52.37]	0.472 / [-4.89]	0.500 / [0.76]	0.500 / [0.85]
0.993	52300	0.801 / [-21.43]	0.980 / [-1.34]	1.005 / [1.17]	0.999 / [0.63]
2.480	125000	2.26 / [-9.44]	2.43 / [-2.18]	2.44 / [-1.45]	2.42 / [-2.37]
5.060	254000	4.84 / [-4.45]	4.99 / [-1.32]	5.00 / [-1.22]	4.95 / [-2.27]
10.125	549000	10.75 / [5.96]	10.86 / [7.05]	10.84 / [6.82]	10.72 / [5.70]
25.313	1250000	24.78 / [-2.11]	24.82 / [-1.99]	24.72 / [-2.36]	24.44 / [-3.52]
49.630	2600000	51.82 / [4.31]	51.68 / [4.05]	51.45 / [3.61]	50.86 / [2.44]
99.267	4920000	98.3 / [-1.01]	97.85 / [-1.44]	97.40 / [-1.90]	96.26 / [-3.08]
Regression	**Slope** $\left(\frac{counts}{ng/mL}\right)$	49940	50250	50500	51100
	Intercept (counts)	12310	3065	1562	1238
	Weight	$1/x^0$ (none)	$1/x^{0.5}$	$1/x^1$	$1/x^2$
Goodness of Fit	r^2 (unitless)	0.99928	0.99927	0.9991	0.9989
	SSE (counts)	1.67E+10	2.60E+09	4.30E+08	2.18E+07
	RMSE (counts)	45727	18031	7331	1650
	$\sum\lvert RPD\rvert$ (%)	2650	82.29	27.09	25.15

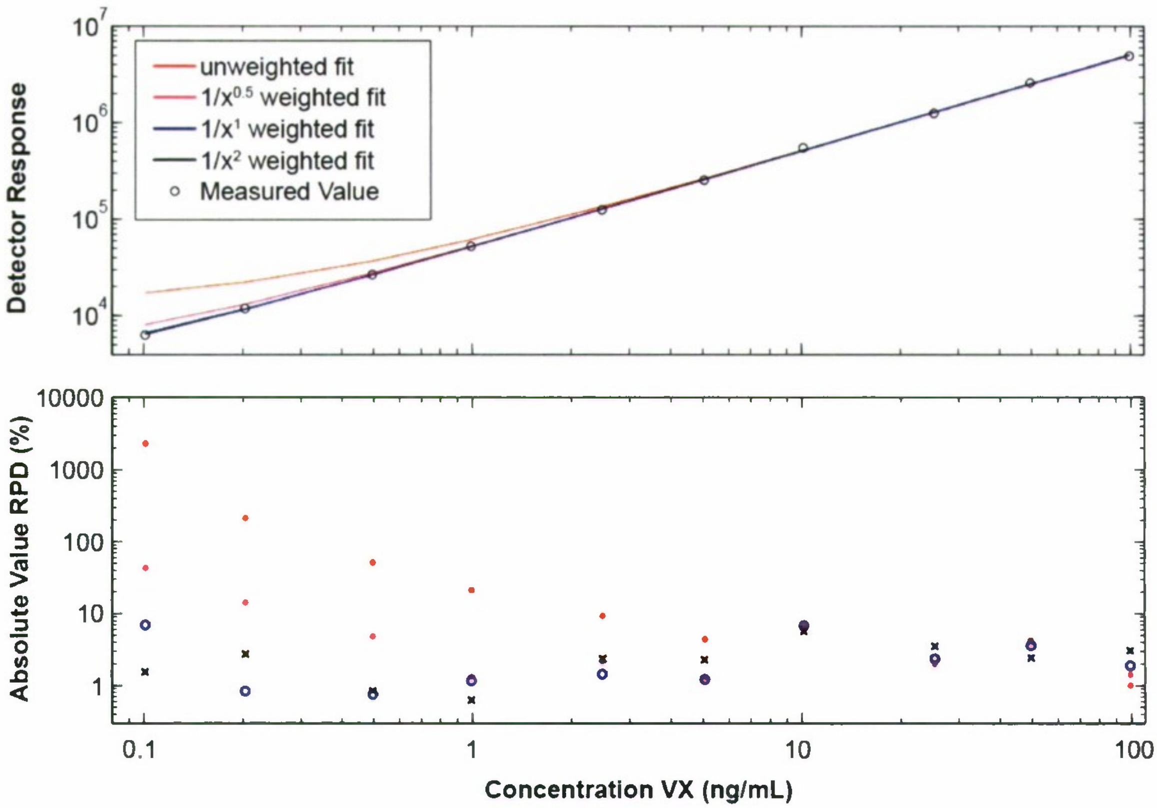

Figure 6H-3. Calibration and RPD graphs for VX with weighting.

Based on the results in Table 6H-2 and Figure 6H-2, the 1/x and 1/x^2 weighted regressions provide the best fit. The next question is which is better to use. At this point, it is recommended to choose the weighting that provides the smallest sum of absolute value of RPDs (Kiser 2004), in this case the 1/x^2 weighting. There are statistical tests that can be used to evaluate calibration curves such as the F-test (or a Mandel Fitting Test); however, caution should be used with applying these tests as equal weighting is assumed for all data points and will likely indicate the unweighted model as the better fit.

Overall, it is suggested that the calibration be reported by providing the known concentrations, the detector responses and the RPD for each standard in addition to the calibration model, weighting, r^2, and coefficients. Acceptance of a calibration curve based on r^2 alone does not imply accuracy, the RPD for every standard should meet an acceptance criteria (e.g., RPD < 15%). Providing all of this information demonstrates the accuracy of the calibration and enables reprocessing of the data if it is determined that an inappropriate calibration model was selected.

Quality Control Samples and Sample Queues: Even with the acquisition of an acceptable calibration curve, there is the possibility that the instrument calibration could drift or change during the analysis of samples. The best way to prevent these issues is to keep the instrument well maintained, however even the best maintained instrument may drift during an analysis. To ensure confidence that accurate results are generated, quality control samples should be analyzed during a run. The order that the standards, analytical samples, and QC samples are run in is referred to as the sample sequence or sample queue (used interchangeably). Most often, the instrument control software calls this order a sequence. Logic should be applied in the organization of the sample queue as effects such as carryover, interferents, or instrument

drift could invalidate large sets of data. The following guidance discusses what each type of QC sample is, what it indicates, how it is used, and finally how the QC samples should be integrated into the sample queue.

Quality control samples are used to ensure confidence in the reported analytical value. QC samples enable trend analysis, determination of bias in sample analysis, detection of instrument drift, carryover, and provide information on the error in the reported analytical value. QC samples include initial concentrate verification (ICVs), continuing concentration verification (CCVs) and blank samples. If the QC samples do not meet performance criteria, it is an indication of a possible problem that must be corrected to ensure confidence in the analytical data.

ICVs are used to verify that a standard of known concentration is accurately determined by the instrument and calibration model. Although not required, an ICV should be a standard that was **not** used to generate the calibration curve. The accuracy of the ICV sample can be calculated using a relative percent deviation (RPD) as defined by

$$RPD_{ICV} = \frac{C_{\text{Calc}} - C_{\text{known}}}{\left(\frac{C_{\text{Calc}} + C_{\text{known}}}{2}\right)} \times 100\%,$$

where

C_{Calc} = concentration/mass calculated from the calibration model,
C_{known} = known concentration/mass of sample.

Acceptance criteria for the ICV should be established, typical values would be in the range of ±15-30% RPD. An ICV with an RPD within the acceptance criteria indicates a successful calibration; failure to meet the ICV acceptance criteria indicates low confidence in the calibration curve and thus low confidence in the data produced from the calibration. ICV samples are typically run shortly after the standards in the queue, discussed later in this document.

The sensitivity of an analytical instrument can change over time for various reasons including: build-up of analyte, presence of interferents from samples, variations in room temperature, or the need to perform maintenance such as changing an injection port septum, conditioning, or replacement of the column. To confirm that the performance of the system does not change (i.e., the calibration changed or drifted) during a sequence, use of continuing calibration verification (CCV) samples is required. A CCV sample is often a rerun of a standard as a confirmation that the measured concentration has not changed, and thus the instrument is performing consistently. This can be accomplished by calculating the RPD of the calculated concentration of the CCV sample (C_{Calc}) to the known concentration (C_{known}) as given by

$$RPD_{CCV} = \frac{C_{Calc} - C_{known}}{\left(\frac{C_{Calc} + C_{known}}{2}\right)} \times 100\%.$$

Acceptance criteria are established to determine if a CCV indicates an acceptance or failure to hold calibration. Typically a value of greater than ±30% RPD is used as failure criteria for a MSD. The variation in concentration/mass of CCV samples is a result of errors from both systematic and random sources. The 30% performance criterion is a commonly accepted standard. If a failure is detected, corrective actions must be taken to return the instrument to

calibration (e.g., instrument maintenance, rerun standards, etc.). Further samples acquired before and after a failed CCV are suspect and will need to be rerun, as discussed later.

It is recommended that more than one concentration be tested as a CCV, selection of which concentrations to use is dependent on the objective of the experiment. Overall, the CCV concentration should correspond to the concentrations expected from the test. It is expected that most decontamination tests will be attempting to meet a requirement, thus it would be advisable to include a CCV near the requirement concentration and one at a mid to high end of calibration. Other government organizations such as the FDA recommend three values corresponding to ~3 times the LOQ, midrange and high range concentrations for CCVs. (FDA 2007) The quality sample and acceptance methods used by a laboratory should be documented in the final report as there are several guides and methods that can be utilized.

The last type of QC sample discussed here is the use of blanks. A blank sample is a sample containing only the extract solvent (or uncontaminated vapor tube). A blank should not elicit a detector response at the expected retention time of the analyte of interest. Blanks are an effective means of evaluating baseline performance and confirming there is no analyte carry-over in the system. Analyte carry-over is the detection of an analyte in one sample that was the result of the analysis of a previous sample. The result of analyte carry-over is a positive bias in a sample, present mostly in low concentration/mass samples. When running a solvent blank, a detector response noted at the expected retention time can be indicative of carry-over of high concentration/mass samples, interferences, a dirty system or other problem that may affect the identification and quantitation of the analyte of interest. Blank samples are included in the sample queue at regular intervals to check for carry-over, as discussed later. The acceptance criteria for the blank or solvent only sample is that the reported concentration must be below the LOD for the analysis method. This criterion was established to ensure that any carryover would not appreciably affect the results of the sample analyzed next in the sequence.

The acquisition of a successful calibration model indicates an instrument that is calibrated under ideal conditions. As samples are analyzed over a period of time (runs can last from 1-36+ hours and include 1-100+ samples), many things could happen to the analytical system that could change the instrument sensitivity and performance, as previously discussed. For this reason QC samples must occur at regular intervals during the sample queue to confirm the analytical instrument is performing within specifications.

In addition to the QC samples, consideration should be applied to the order that the samples are run. In decontamination testing some samples may have concentrations that are significantly different (e.g., the contact-test for a bare metal vs. an elastomer). If there is any carry-over in a system, a very high concentration sample followed by a low concentration sample could yield a false high (i.e., positive bias) concentration in the low concentration sample. For this reason it is advisable for the operator to use best judgment in the organization of samples to prevent this situation. In addition to the sample concentration, some samples are 'cleaner' than others. For example, the contact test involves the extraction of a contact sampler that has been acetone rinsed to remove impurities. This extraction is relatively clean in that the only compounds in the extract solution are likely the agent and possibly some agent reaction byproducts. In comparison, residual agent extractions are in some cases not 'clean' in that the extraction process may have removed other compounds from the coupon (e.g., plasticizers extracted from elastomers like silicone). It is possible that some interferents extracted from the coupons may alter the performance of the analytical instrumentation (e.g., interferents coating the column), this could be detected by failing CCVs or positive blanks. To minimize rerunning large numbers of samples it is advisable to put samples that are 'dirty' or likely to contain impurities together at

the end of a queue. If the interferents are significant enough, sample clean-up procedures (e.g., solid phase extraction) may be needed to accurately analyze the samples and prevent damaging the analytical instrumentation (e.g., destroying the column). In summary, it is best to run the 'cleanest' samples first and order the samples from anticipated lowest concentration to highest concentration.

In most cases a queue is initiated with a series of blanks followed by the standards, another blank, an ICV, a CCV block, then samples, with iterations of CCV blocks and samples until the queue is complete, terminating with a CCV block. Figure 6H-4 provides a demonstrative sample queue. The first blank ensures that the system is 'warmed' up and flushed out, the second blank can be used to verify the system is clean and there is no carry over from previous runs. The standards are then run from lowest to highest concentration (minimizing the effect of any potential carry-over). The blank run after the highest standard is primarily used to detect any carry-over in the system. Because this blank follows the highest concentration anticipated to be run in this sequence, if carry-over is occurring it will be reflected in this sample. The ICV sample is then run to confirm that an acceptable calibration was acquired.

After the ICV, the following sample begins a CCV block. In this example a CCV block consists of a blank, a low level CCV (1 ng/mL) and a mid level CCV (50 ng/mL). After a CCV block, a set of samples is run, followed by another CCV block. The CCVs surrounding the samples are said to 'bracket' the samples. For a set of samples to be accepted both bracketing CCV blocks must pass. In the event of a QC sample failing to meet an acceptance criteria (e.g., blank detecting carryover or CCV > 30% RPD), the samples preceding and following the CCV block are suspect and should be rerun. It is not possible to identify when the instrument was failing to meet specifications, thus all samples between the last passing QC sample and the failing sample should be rerun. In addition to this guidance, other documents such as Chapter 9 of the US Army Engineering Manual EM200-1-10 can be used to accept or reject data.

The frequency of CCV blocks is a balance of instrument run time and confidence in instrument performance. For example, given the frequency of nine samples per CCV block, the failure of one CCV block would dictate that 18 samples are rerun (the samples before and after the failing CCV block). Selecting a large number of samples between CCV blocks results in a shorter total queue run-time, however, a CCV block failure results in a significant number of samples to rerun. Conversely, running a CCV block between every sample is also not practical. Typical intervals for CCV blocks are 5-20 samples. If particular samples are expected to cause instrumentation problems, or extra confidence is desired, CCV blocks can be run more often.

Queue Number	Sample Type	Known Conc. (ng/ml)	Sample Name
1	blank	0.0	blank00
2	blank	0.0	blank01
3	std	0.1	0.1std
4	std	0.2	0.2std
5	std	0.5	0.5std
6	std	1	1std
7	std	2.5	2.5std
8	std	5	5std
9	std	10	10std
10	std	25	25std
11	std	50	50std
12	std	100	100std
13	blank	0	blank02
14	ICV	7	7ICV
15	blank	0	blank03
16	CCV	1	1CCV1
17	CCV	50	50CCV1
18	sample		sample1
19	sample		sample2
20	sample		sample3
21	sample		sample4
22	sample		sample5
23	sample		sample6
24	sample		sample7
25	sample		sample8
26	sample		sample9
27	blank	0	blank04
28	CCV	1	1CCV2
29	CCV	50	50CCV2
30	sample		sample10
⋮			⋮

Comments:

Ensure 'warm up' and 'clean' system.

Run Standards

Check for carry-over

Check ICV

Test blank and CCVs

Samples 1-9 are bracketed by CCVs 1 and 2

Test blank and CCVs

Green = QC Sample

Blue = Standards

Black = Samples

Figure 6H-4. Example analytical queue with QC samples

REPORTING

The following information must be documented in the test report for this procedure. Most of the required reporting information can be captured in the experimental section.

The experimental section should include a description of the analytical equipment used including configuration and software operating platform. The report should contain a description of the analytical methods used including the calibration range, calibration standard preparation, calibration model, calibration weighting, limit of detection, limit of quantitation, quant ions used, column. The report should also include a description of the quality control and assurance procedures such as use of initial and continuous calibration samples (ICV, CCV) and solvent blanks; non-detect, below-detect and below quantitation result reporting criteria; sample dilution

procedures; and data acceptance criteria. For most reports, this information may be best captured in the experimental and referred to in the test result and discussion sections.

Test data collected outside the calibrated range should be documented as such. A non-detect (ND) should only be reported when a true non-detect is observed. Sample analysis identifying agent present below the method calibration limit or quantitation limit should be reported as below detection (BD) or below quantitation (BQ) as appropriate. An estimated quant value can be provided, but should be documented indicating that the value is an estimate and below method detection or quantitation. The analysis of extract samples resulting in values above the calibration range can typically be diluted to enable analysis within the analytical method range. Results should be clearly noted so that unfamiliar readers do not incorrectly assume that a result is suspect because it is greater than the analytical method calibration range.

REVISION HISTORY

March 2008: original method.

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Section 7: Panel Vapor Test to Determine Vapor Hazard

DESCRIPTION

The vapor test series contains the procedures for the measurement of agent vapor present after the decontamination process that could pose a vapor hazard to unprotected personnel. These tests utilize a vapor collection system to capture coupon off-gassing and chromatographic analytical methods. The rigorous laboratory-scale test method uses a standard a two inch diameter circular coupon. The methods can be applied to larger coupons and test articles. These tests evaluate liquid agent challenges against decontaminants in liquid-, solid- or vapor form. The experimental test data can be converted to a vapor hazard value in units of mg/m^3.

CONTENTS

7A - Laboratory-Scale Decontaminant Performance Evaluation for Vapor Test Method

7B - Rinsate Analysis for Agent Test Method[1]

7C - Baseline Vapor Test Method

7D - Panel (Coupon) Extraction Efficiency Test Method

7E - Data Calculation Method to Report Vapor Hazard

7F - Chromatographic Analysis Guidance

NOTES

[1] Denotes method being developed as part of FY08 effort for program CA07DEC420.

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Test Procedure 7-A: Laboratory-Scale Decontaminant Performance Evaluation for Vapor Test Method

SUMMARY OF PROCEDURE

The vapor test is the measure of the emission factor of the contaminant from the test material after the decontamination process that could pose a hazard to unprotected personnel. Samples are placed in vapor chambers and air is passed over the sample and collected onto a solid sorbent tube. The agent collected on the tube is thermally desorbed and analyzed. **The laboratory-scale Decontamination Performance Evaluation for vapor-hazard measurement is a rigorous method for the execution of decontamination testing using a standard two inch disk coupon.** This method can be used to evaluate decontaminant performance against liquid-phase contaminants such as chemical-warfare agents, chemical-warfare agent simulants, toxic-industrial-chemicals and toxic-industrial-materials. The terms contaminant and agent are used interchangeably.

This procedure provides the following information:

- **The mass of agent in nanograms recovered from the solid sorbent tube after the decontamination process.**
- **The mass of agent in nanograms recovered from the coupon after the decontamination process and vapor test**

The following prerequisite tests are required for this test procedure:

- Procedure 7-D, "Panel (Coupon) Extraction Efficiency Test Method" is the method for determining the efficiency the selected solvent has for recovering agent from the coupon.
- Procedure 7-H, "Chromatographic Analysis Guidance is the guidance protocol for the analytical analysis of the extracts generated in this test.

This procedure alone does not provide the complete assessment of the decontaminant's performance for reducing the agent contamination or reporting the hazard. The complete assessment of decontaminant performance should also address:

- The amount of agent physically removed from the coupon during the decontamination process using either liquid decontaminants or post-decontamination rinsing step.
  - Procedure 7-B, "Rinsate Analysis for Agent Test Method" is the measurement of the amount of agent physically removed from the coupon during the decontamination process.
- The amount of agent lost during the decontamination process to weathering / evaporation.
  - Procedure 7-C, "Baseline Vapor Test Method," is the method for conducting the decontamination process without the use of decontaminant.
- Reporting the vapor hazard value in mg/m^3.
  - Procedure 7-E, "Data Calculation Method to Report Vapor Hazard" is the process for converting the mass of agent recovered from the sorbent tubes to a reported hazard value.

Limitations and other test variations:

- The collection of vapor data is not a direct measure for percent efficacy, percent neutralization, or reduction in starting challenge. These measurements must be conducted using the appropriate procedures in Chapter 6.
- **Contaminant Simulant:** Chemical compounds for chemical agents are often used during early screening or at non-chemical agent surety facilities. A chemical agent simulant is a chemical compound of lower toxicity than the chemical agent with at least one property similar to the chemical agent such as certain bonding, functional group, physical property, etc. Simulants should be selected based on the main property being tested for the most accurate comparison. Since simulants do not contain all of the same physical and chemical properties of the live agent; simulant data alone is not sufficient to determine decontaminant performance. It is recommended that the simulant performance be confirmed with agent data.
- Bagging and sampling is not an appropriate method to determine a vapor hazard. Bag and sample methods can give an indication if offgassing may be present but due to uncharacterized air flow and uncontrolled volume the measurement cannot provide an accurate assessment of hazard.
- Certain variations fall outside the scope of the Laboratory-Scale Performance Evaluation test methods. This vapor test is directly applicable to items that can be placed in appropriate vapor chambers. However, the residual agent measurement is only directly applicable to panels, items or other test surfaces that can be extracted in solvent.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air. In this case the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample -** liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **breadboard, brassboard, prototype** – technology in differing degrees of configuration still under development that is not in final form. This can apply to test fixtures, formulations and/or the decontamination system / applicator.
- **chemical agent** - a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contaminant -** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical and toxic industrial materials. A list of contaminants is provided in Appendix B.

- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant -** for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process** - the process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically for these procedures, the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing and drying.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample –** a sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction –** the separation of a component from a mixture through selective solubility.
- **extraction efficiency -** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **hazard -** A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*

- **moderate condition** - test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **nonsorptive materials** - a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **operational decontamination** – decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material and/or working areas, in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate** - the collected rinse from the decontamination process. The sample may include residual decontaminant, agent, or agent byproducts in water.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface, if the droplet significantly spreads across the surface it is better described as a thin film.
- **sorptive or porous materials**: a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition** - for a specific agent – material- decontaminant set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **vapor chamber** – a dynamic vapor microchamber that fully encloses a coupon to enable vapor emission analysis. The chamber must facilitate the ability to control air flow and mixing, collect vapor samples, and measure environmental conditions such as temperature and relative humidity.
- **vapor cell** – a dynamic vapor enclosure that is placed over the surface to be tested for vapor emission analysis. The tested surface serves as one of the 'walls' of the enclosure. The use of a vapor cell is not within the methods described here.

- **vapor hazard** – a value specified in requirements documents usually specified as a concentration (mg/m^3) that should have an accompanying exposure time. The value corresponds to an exposure that presents an acceptable risk level for to unprotected personnel exposed to the vapor concentration. The toxic load model should be applied to calculate a vapor hazard.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-5, Nuclear, Biological, and Chemical (NBC) Decontamination, 17 November 1993.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.5, Multiservice Tactics, Techniques, and Procedures for Chemical, Biological, Radiological, and Nuclear Decontamination Nuclear, Biological, and Chemical (NBC) Decontamination, 4 April 2006
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.9, Potential Military Chemical/Biological Agents and Compounds, 10 January 2005.
- Headquarters, Department of the Army (DA), Washington, DC, Army Manual (AR) 70-38, Research, Development, Test and Evaluation of Materiel for Extreme Climatic Conditions, 15 September 1979.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.
- American Society for Testing and Materials (ASTM), Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air, ASTM Document Number D 6196.
- American Society for Testing and Materials (ASTM), Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products, ASTM Document Number D 5116.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
    - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
    - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
    - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Decontaminants:** The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid- or vapor-phase and may contain a reactive functionality for neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Extraction solvents:** The residual agent test requires the extraction of agent sorbed into the coupon during testing. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride and solvent blends.
- **Water:** Decontamination processes typically involve a post-rinse step and some decontaminants are made using water. Laboratory testing will use distilled or deionized water unless otherwise instructed by the test sponsor.

EQUIPMENT

The equipment required for this method includes tools for delivering the contaminant, decontaminant and rinse water; and maintaining environmental control and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision, and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly, and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant

volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 µL which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 µL delivered as two 1 µL drops for a 1 g/m^2 starting challenge.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips are preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions, or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. These are also best suited for pipetting volatile liquids. The smallest delivery volume, based on a survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
- Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. Smallest delivery volume based on survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
- Computerized Dispensing System: Automated tool with ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.

- **Decontaminant Delivery Tool:** the tool used to deliver a specific volume of decontaminant to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The core coupon test specifies using a decontaminant volume of 1.00 mL. The specific decontaminant under evaluation may use other delivery volumes.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of decontaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
    - Spray Bottle: Some applications will mimic a spray application using a spray bottle. The tool should be evaluated to determine the number of pumping actions required to achieve target decontaminant application. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.
    - Developmental Breadboard, Brassboard or Protoype Technology: These are technologies under development that are not in final configuration. The

decontaminant generation and delivery may not be known. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- Vendor Provided Technology: This is equipment provided from vendor that may be breadboard, brassboard, prototype or commercial in configuration. The technology is operated per vendor guidance. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Water Rinse Delivery Tool:** Tool for the delivery of specific volumes of water to the coupon surface to remove decontaminant from the surface. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. Recommended that tool used has ability to control flow rate to reduce operator-to-operator variations. The typical delivery volume for a 2 in. diameter circular contamination area range is 60 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. An example is the Dispensette and Brinkman brands. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
  - Pump: Other precision liquid dispensing systems. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume.

Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.

  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
  - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.

- **Environmental Chamber:** Temperature and relative humidity controlled chamber for the preconditioning and aging coupons. The fixture should be able to maintain test specific environmental conditions (e.g., temperature and relative humidity) even when adding or removing samples. The system must have temperature and relative humidity data logger capability, be able to store and download temperature and humidity data and traces to a computer for further analysis. The system must be able to maintain temperature and relative humidity. The system operation and range should be known.
- **Contaminated Area Measurement:** Fixed-site photographic setup to visually capture the agent contamination surface area coverage after dosing, aging and any other critical steps in the decontamination process. Photograph resolution of 9 to 25 pixels per droplet measured is recommended for surface area calculations.
  - Digital Camera on Fixed Stand
  - Imaging Station
- **Vapor Chamber:** An enclosed structure of sufficient size that completely contains the coupon/test article with the following requirements. General guidance for vapor chamber construction can be located in ASTM D 5116-06 "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products." Several considerations for decontaminant evaluations are provided in the bulleted list.
  - The chamber should be constructed of inert materials.
  - The chamber should ideally run under positive pressure to minimize contamination inside the chamber.
  - The vapor chamber must have a clean air supply with tight control of the chamber air flow rate (±5% minimum).
    - Mass flow controllers or mass flow meters are preferred over volumetric flow meters (requires standard temperature and pressure (STP) correction).
  - The chamber should have the ability to measure temperature and humidity, control of temperature and humidity are ideal.
  - The chamber should provide a well mixed environment.
  - The volume of the chamber must be known.
  - The chamber must have an exhaust port to enable collection of vapor samples.
  - The sampling air flow must be known.

- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Procedures 7-F and 7-G. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the coupon. A glass container such as a vial or jar of sufficient size to hold both the coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommended for chemical agent testing.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** are typically used during the aging step to cover the coupon surface to minimize evaporative loss. Can also be used as sample holder.
- **Rinsate collection container:** If rinse water analysis is required, the rinse should be collected in a glass container of sufficient volume for the rinse water and extraction solvent, preferably a wide mouth jar. It is recommended to limit use of funnels or other tools that may uptake agent during collection. Use of plastic containers is not recommended for chemical agent testing. The container cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **Transfer pipettes**
- **Timing device(s):** Test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Solid sorbent tubes:** a tube such as a depo area air monitoring (DAAM) tube that contains a solid sorbent that absorbs the contaminant. Typical solid sorbents include Tenax, Chromasorb or Haysep. The appropriate sorbent should be used for the contaminant being tested. ASTM method D 6196 "Practice for Selection of Sorbents, Sampling, and Thermal Desorption analysis Procedures for Volatile Organic Compounds in Air" provides detailed guidance for the selection of the appropriate sorbent tube.

- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, pH meter.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE – BREAKTHROUGH

Breakthrough is the result of weak analyte and sorbent interactions that as a function of air volume, temperature and flow rate could result in lack of analyte retention in the sorbent. It is vital to ensure that the sampling methodology avoids collecting samples that may experience breakthrough as this would result in underestimating the vapor concentration (and ultimately lead to underestimating the hazard). Even with strong analyte-sorbent interactions breakthrough can occur as a function of the volume of air passed through the tube, the temperature, and air flow rate. This procedure should be conducted for each analyte-sorbent pair of interest with the sampling method used. Most preferably, the test should be conducted at the harshest condition (e.g., highest temperature and flow rate) to be studied. If breakthrough does not occur at the harshest condition, then breakthrough will not occur at ambient case. This procedure only needs to be repeated when new analytes, different sorbents or different sampling methods (e.g., air volume, air flow rate and higher temperatures) are used. This procedure will identify the 'safe sample volume' (SSV) which indicates the maximum volume of air that should be sampled during an experiment.

Users of this method should refer to the following documents for detailed background and guidance regarding breakthrough determinations. A general procedure is provided in this section specific to typical decontaminant vapor testing.

- ASTM method D 6196 "Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air."
- EPA *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* second edition dated 1999. Compendium Method TO-17, Section 10.8.

This test uses two solid sorbent tubes. The first tube in line is referred to as the "spiked tube". A second tube is connected 'down wind' via an appropriate union fitting to the first tube and is referred to as the "breakthrough tube". This test will measure if breakthrough occurred. The mass of analyte detected on the second sorbent tube (i.e., the breakthrough tube) is referred to as the breakthrough mass. The breakthrough volume is defined as the volume of air passed through the spiked tube which results in a breakthrough mass that is approximately 5% of the delivered mass. The safe sample volume is defined as 70% of the breakthrough volume per ASTM D 6196. The general breakthrough test procedure is:

1. Spike the spiked tube with a known mass. This mass on tube should represent the high end of the method calibration curve used to analyze samples. If a laboratory has multiple methods, recommend performed this test using the highest range curve.
2. Connect the spiked tube and breakthrough tube to the vapor chamber where samples are typically collected.
3. Run the empty vapor chamber at the desired operating air flow rate, total air volume and temperature for a specified period of time. Recommendation is to use a sampling time twice the length of the desired sampling time.
4. Analyze both tubes using the analytical techniques specified in Method 7-G.
5. If 5% of the delivered mass is recovered on the breakthrough tube, breakthrough has occurred. A safe sampling volume would be 70% the air volume used. For example, if the breakthrough test used a 120-min. pull time resulting in 5% breakthrough, then an 84-min. pull time can be used for testing without changing the air flow rate or temperature.
    - Note: if greater than 5% breakthrough is observed, the safe sampling volume will be less than 70% of the air volume used. A second test with adjusted parameters would be required to determine the parameters generating a 5% breakthrough so that the SSV could be determined.
6. If the SSV is significantly small, the following guidance should be considered to enable decontaminant vapor testing and emission factor calculations:
    - Consider a different sorbent.
    - Consider a lower tube loading (i.e., less mass on tube).
7. To ensure that breakthrough has not occurred at the final air flow rate, air volume and temperature operating conditions, a final test at the desired pull time should be performed to confirm that breakthrough does not occur.

PROCEDURE – VAPOR SAMPLING PLAN DEVELOPMENT

The vapor test experiment duration should be no shorter than 6 hr, and more preferably 12 hr. The use of extremely short experiment durations could limit the ability to properly characterize the emission source and the potential for data extrapolation. The planning process requires a bit of trial and error. The objective of this section is to determine the tube midpoint time and start time, and for low long to sample, the tube pull time, for each vapor tube. The objective for the vapor sampling plan is to provide a sampling schedule that will load each tube with an analyte mass that can be detected by the analytical method without saturating the detector from long sampling times, or resulting in mass loading below the analytical method from short sample times.

The selection of tube midpoint times and tube pull times is a combination of the vapor chamber operating parameters (e.g., air flow rate, air volume, and temperature), safe sample volume (determined by the breakthrough test), the sample under investigation and the analytical method calibration range. The steps provided are general guidance to enable the user to determine the schedule for their system. An example microchamber vapor sampling plan is used in this procedure. The example uses a decontaminated coupon placed in a microchamber sampled with six sorbent tubes over the course of 6 hr at ambient temperature. The example uses a 36 mL vapor chamber with a 300 mL/min flow rate. For a set sampling flow rate, there is a

maximum sampling time that will correspond to the SSV determined by SSV divided by the sampling flow. Sampling longer than this maximum pull time will result in breakthrough. The example uses maximum sampling time of 60 min. The example planning results are shown in italicized text, Tables 7A-1 and 7A-2 and Figure 7A-1.

1. **Determine the air change rate**: the air change rate is the chamber air flow rate divided by the chamber free volume (e.g., total volume minus coupon volume).
2. **Determine the suggested first sample start pull time**: The guidance for constant emission sources is to determine when the chamber will reach an equilibrium concentration. A general equation that can be used to select this first point is

   Initial tube start time = 2.3 / air change rate

   - Microchamber notes: the use of micro chambers may give an oddly low result in fractions of a minute. For this case collect the first sample starting at 5-min into the vapor sample time.
   - Larger chamber notes: This equation applied to larger chambers provides guidance regarding the amount of time required to reach equilibrium in an ideal case (e.g., constant emission). The first tube pull should start at the calculated initial time.
3. **Vapor profile working assumption**: The working assumption for the evaluation of decontaminated samples is that the vapor concentration is expected to decrease over time. The resulting vapor profile plotted as concentration versus time would produce an exponential decay curve.
4. **Select the last sample tube pull time**: This test method is for the evaluation of samples that have been decontaminated. It is expected that the last sample will contain the lowest concentration. The last tube is collected such that the end time is the end of the vapor sampling period. The total sample collection time is the time determined by the breakthrough evaluation safe sample time.
   - *Example: breakthrough study determined that for the microchamber operating conditions that the maximum sample pull time is 60-min. The last sample would be collected starting at 300-min through 360-min for the 6-hr test.*
5. **Determine remaining sample distribution**: These are initially selected to sample over the entire test duration with greater emphasis in the first 3-hr of sampling. The midpoint sample time is determined in this case.
   - *Example: tubes 2, 3, 4, and 5 are spaced at midpoint times 30, 75,135 and 225 minutes over the course of the vapor period.*
6. **Determine initial test length of sample collection**: Establishing the initial pull values is dependent on the specific chamber used and the analytical method calibration range. General guidance is to use short pull times so that tube saturation does not occur. In addition, the tube time should not be so short that the mass collected cannot be quantified. Experience with the specific vapor chamber and analytical equipment should be used if known. If this information is not known, a starting point is the use of sample collection times ≤ ¼ of the maximum sampling time within the first 3-hours of testing and ≥ ½ the maximum sampling time for the latter sample times.

- *Example: In order to prevent saturation for the first two tubes, a 4-min sample pull time was selected. The pull time for tubes 3 and 4 was initially set at 16 minutes.*

7. **Create an initial sampling time table**: Create an initial sample table with the start, end, pull and midpoint times.

Table 7A-1: Initial tube sampling time example table.

Tube #	***Start Time (min.)***	***End Time (min.)***	***A. Pull time (min.)***	***Midpoint Time (min.)***
1	*5*	*9*	*4*	*7*
2	*28*	*32*	*4*	*30*
3	*67*	*83*	*16*	*75*
4	*127*	*143*	*16*	*135*
5	*210*	*240*	*30*	*225*
6	*300*	*360*	*60*	*330*

8. **Run test and adjust timing as needed**: Vapor sampling requires some scoping work to determine the best combination of parameters. The initial test may identify the need to reduce sample times to prevent tube saturation or exceeding analytical calibration limits.
   - Note: the slope of the curve determines if points need to be moved earlier (e.g., steep decay curves) or move out longer in time (e.g., slow decay curves). If the majority of data points are moved early to support steep decay curves, the last tube should be collected at the end of the vapor test sample duration even if it is a zero value so that the test was carried out through the entire time.
   - *Example: For this particular example, pull times that were multiples of 5-min were preferred. The pull times that best sampled the coupon vapor emission were selected and the table updated for the full test (Table 7A-2). The table is shown visually in Figure 7A-1.*

Table 7A-2: Final tube sampling time example table.

Tube #	***Start Time (min.)***	***End Time (min.)***	***Pull time (min.)***	***Midpoint Time (min.)***
1	*5*	*10*	*5*	*7.5*
2	*25*	*30*	*5*	*27.5*
3	*70*	*80*	*10*	*75*
4	*130*	*145*	*15*	*137.5*
5	*215*	*240*	*25*	*227.5*
6	*300*	*360*	*60*	*330*

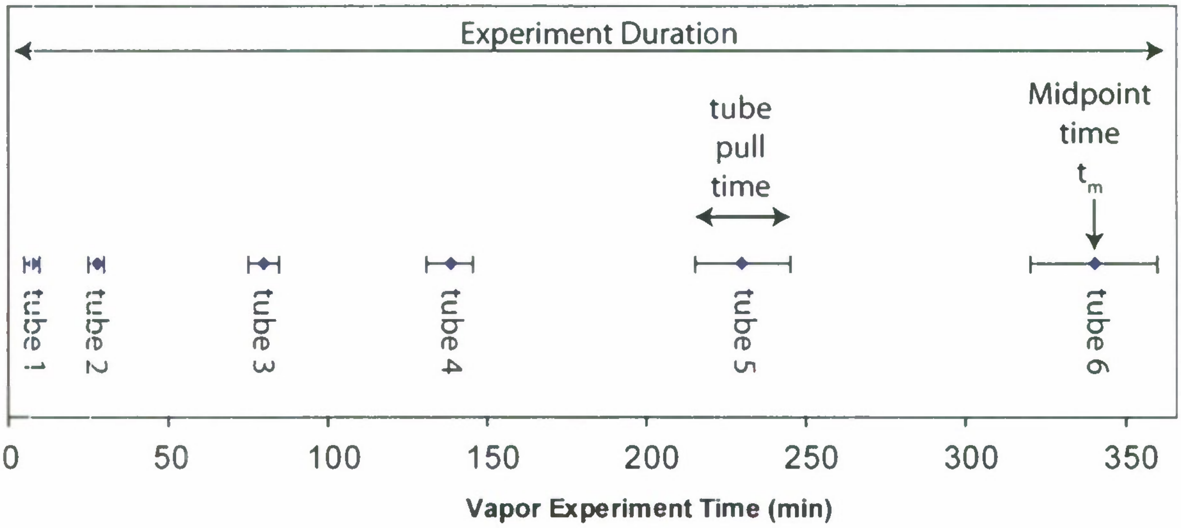

Figure 7A-1: Graphical representation of the tube pulling schedule.

PROCEDURE – VAPOR TEST

The procedure specifies the sample handling, measurement and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.

This test has Options A, B and C that are step variations based on potential variables that could be explored. The core test evaluation is designated by Option A. This option is based on a liquid decontaminant tested at moderate environmental conditions using equipment with known accuracy. This option should be used unless otherwise instructed by a test sponsor. Option B is similar to Option A but allows for different parameters, such as temperature. Option C is designed for the evaluation of new technologies or the use of conditions outside of the core test. The use of lettering does not indicate a test grade. The letter serves as a quick reference to the selections made during testing and the considerations required for comparing different groups of data. Option A and B parameter choices are preferred in cases where lab-data must be compared to requirements; however, Option C parameters may need to be used, especially for the evaluation of new technologies.

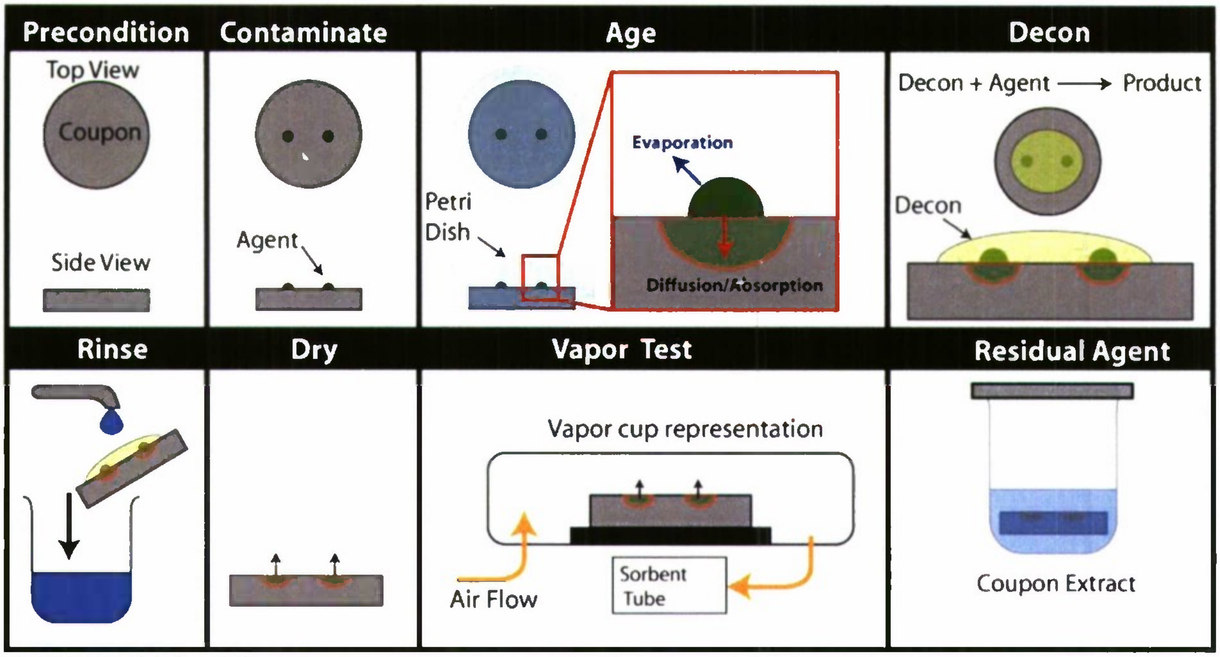

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Figure 7A-2. Vapor Test Representation.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- **Identify the calculation desired. Review the Calculation Procedure 7-E and select appropriate test methods and options within a test method to ensure the necessary data is collected.**
- Turning on equipment that will need to thermally equilibrate (i.e., environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars) and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Prepare decontaminant.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- Recommended that contaminant equilibrate to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, and rinse times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of 5 coupons per test condition and 3 dose-confirmation samples per contamination set.

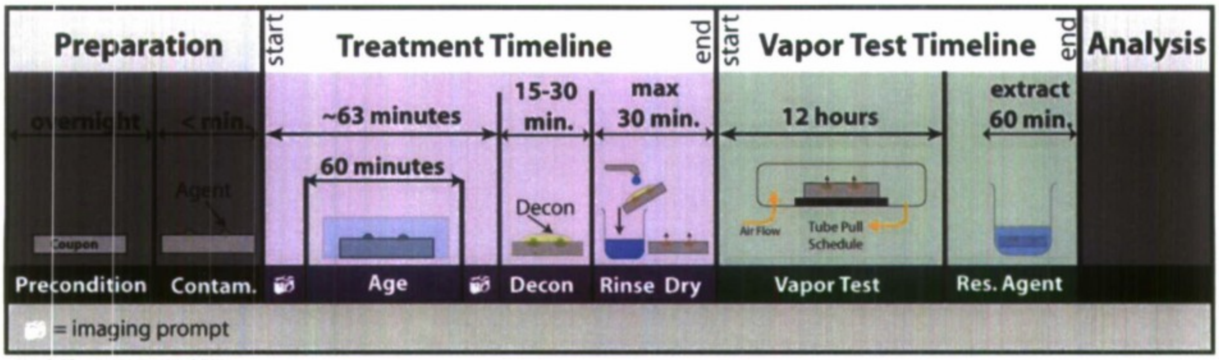

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Figure 7A-3. Vapor Test Timeline Representation for Option A.

2.0 Precondition Coupons

2.1 Set the environmental chamber to the specified test condition

<u>OPTION A (core test)</u>: moderate condition test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported.

<u>OPTION B (core test, variable condition)</u>: variable condition test with environmental chamber using test sponsor / director temperature and relative humidity set-point. Most common test cases are high and low temperature and relative humidity.

<u>OPTION C (outside core test)</u>: test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

2.2 Allow environmental chamber to equilibrate at the set-point temperature and relative humidity. The time to reach set-point equilibration may vary based on equipment and set-point conditions. Recommended that temperature and humidity are maintained at the set-point for at least 30 min prior to the start of conditioning.

2.3 The coupons are placed horizontally on coupon trays with the test surface to be contaminated / decontaminated facing upwards.

2.4 Once the chamber has equilibrated at the set-point temperature and relative humidity, place the trays into the environmental chamber for at least 60 min. Recommended practice if possible is to precondition the test materials overnight.

- Note: some materials may require special preconditioning treatments. For example, cellulose based materials and concrete contain significant moisture. These types of materials do not typically achieve moisture equilibrium in less than 24 to 48 hours. Longer precondition times may be required for certain materials. An example procedure for wood is ASTM D4442.

2.5 Samples should not be removed until ready to execute Step 3 Contaminate Coupons.

2.6 Complete the required reporting for this section.

3.0 Contaminate Coupons

3.1 Identify contamination density to include number of drops, drop volume and deposition pattern.

OPTION A (core test): contamination density is 1-1.2 g/m^2 applied using pipette / syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): variable contamination density is typically between 1 to 10 g/m^2 applied using pipette / syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

OPTION C (outside core test): application of agent using brushes, rollers or sprays applicators such that the amount of agent applied to the specific surface is not tightly quantifiable. Note: calculation of percent neutralization might not be feasible using this option.

3.2 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with clean, appropriate pipette tip

3.4 Load contaminant delivery tool in accordance with manufacture's directions.

3.5 Deliver to the surface the appropriate number of drops to achieve the contamination density. Reload the tool and repeat as needed for total number of coupons. Treatment time starts after coupon is contaminated. Recommended use of timing charts for multiple samples.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests) or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.6 If using pipettes or syringes to deliver contaminant, prepare the "dose confirmation" sample. At least three replicate samples are recommended.

3.6.1 Delivering to a scintillation vial the appropriate number of drops to achieve the contamination density.

3.6.2 Add 20 mL of extraction solvent.

3.6.3 Cap vial

3.6.4 Thoroughly mix contents by inverting vial three times.

3.6.5 Using a clean, disposable pipette load the analytical vial with aliquot of extractant solution.

3.7 Observe the post-contamination drop interaction with the surface and surface coverage.

OPTION A (core test): using digital camera or imaging station, photograph each coupon surface.

OPTION B (core test variable condition): some materials may not allow for the rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three independent coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered documented both in words and hand drawing.

3.8 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

3.9 Complete the required reporting for this section.

4.0 Coupon Aging

4.1 Coupons are aged.

OPTION A (core test): Coupons are aged in environmental chamber for 60 min at moderate condition test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported Environmental chamber should have logging capability for real-time temperature and humidity recording.

OPTION B (core test, variable condition): Coupons are aged in environmental chamber under one or more of the following cases. The environmental chamber should have logging capability for real-time temperature and humidity recording.

- Variable temperature and relative humidity: aging conducted at test sponsor / director designated temperature and relative humidity.
- Variable aging time: shorter aging time for immediate or operational decontaminant applications, or aging period longer than the Option A basic thorough test. The aging may be at the moderate condition and/or variable temperature and relative humidity.

OPTION C (outside core test): test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

4.2 Observe the post-aging drop interaction with the surface and surface coverage. (If no aging period is used, this step can be skipped).

OPTION A (core test): using digital camera or imaging station, photograph each coupon surface. There is a chance for some materials the post aging image may not be visible without use of color indicator or dye.

OPTION B (core test variable condition): some materials may not allow for the rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered documented both in words and hand drawing.

4.3 Complete the required reporting for this section.

4.4 Coupons are moved to decontamination test area at end of aging period.

5.0 Pre-rinse the Coupons

5.1 Coupons are rinsed.

OPTION A (core test): pre-rinse is not used for the core test.

OPTION B (core test variable condition): Pre-rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for process and

analysis under Procedure 7-F. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION C (outside core test): the use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement.

5.2 Complete the required reporting for this section.

6.0 Decontaminate the Coupons

6.1 Apply decontaminant

OPTION A (core test): For the core test there are a few sub-options based on the test objective. The decontaminants are liquid-phase and applied using a pipette. Dispensettes or pumps may fall under Option A if the decontaminant delivery volume to the contaminated region can be accurately measured. Unless otherwise specified, the decontaminant applied is typically at room conditions. The amount of decontaminant applied is based on the following guidance.

- Option A-1: For early research tests, it is recommended that 1.00 mL of decontaminant is evenly dispensed over the contaminated coupon surface in a single application. Care should be taken to ensure that the decontaminant is delivered uniformly over the test area. This recommended decontaminant volume is for starting challenges in the 1 to 10 g/m^2 range to ensure that decontaminant covers the contaminated surface area. Some agent-material interactions could result in significant contaminated surface coverage that smaller decontaminant volumes may not be able to adequately cover the entire contaminated surface yielding data scatter due to decontaminant delivery.
- Option A-2: FM 3-11.5 recommends a decontaminant to contaminant ratio of 50:1. This corresponds to 0.100 mL to 1.000 mL for a 1 to 10 g/m^2 starting challenge, respectively.

OPTION B (core test variable condition): Some liquid-phase decontaminants may require applying more or less decontaminant. For vapor-phase decontaminants apply appropriate fumigant concentration.

OPTION C (outside core test): the use of solid decontaminants, sorbent wipes, brushing or mechanical scrubbing methods are outside the scope. These materials have the potential to retain or physically relocate agent. The use of these methods requires adjustment to calculating percent neutralization. Breadboard, Brassboard, Prototype or vendor provided equipment with specified application processes falls here, decontaminant is applied as best as possible in accordance with technology operating procedures.

6.2 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

6.3 Wait appropriate decontaminant residence time at specified environmental condition

OPTION A (core test): standard decontaminant residence time is from 15 to 30 min for liquid-phase decontaminants in environmental chamber at ambient condition test using environmental chamber set to 21 ± 3 °C (70 ± 3 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported. Environmental chamber should have charting capability for real-time temperature and humidity logging.

OPTION B (core test variable condition): liquid-phase decontaminants outside the 15- to 30-minute range or at variable temperature or humidity that are placed in environmental chamber for residence period.

OPTION C (outside core test): liquid phase decontaminants evaluated at room condition. Sorbents and wipes may have other residence times on surface. Vapor-phase decontaminants may dictate environmental conditions as part of process. Breadboard, Brassboard, Prototype or vendor provided equipment with specified application processes using residence times outside the core 15 to 30 min or environmental conditions outside specified test conditions fall here.

6.4 Complete the required reporting for this section.

7.0 Post-Rinse and Dry

7.1 Coupons are rinsed.

OPTION A (core test): Rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for process and analysis under Procedure 7-F. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION B (core test variable condition): Rinse is not collected or analyzed.

OPTION C (outside core test): the use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement. Some decontaminants do not require a post rinse. The impact of residual decontaminant on the analytical measurements must be evaluated.

7.2 Coupon drying

OPTION A (core test): Passive drying is recommended at room conditions, preferably in a chemical fume hood (or equivalent) with approximately 100 linear feet per minute (lfm) airflow. The coupons are recommended to be placed at and angle to increase air flow over surface. Coupons should not be dried for more than 30 min. Residual water on surface should be noted. For most applications wicking the last bead of rinse water should have little impact on the results.

OPTION B (core test variable condition): Controlled air drying which is an active blowing with established air temperature, flow rate, etc.

OPTION C (outside core test): Blotting, wiping or other direct surface contact methods that may also remove agent as part of the process. These methods can impact vapor measurement. No drying would also fall here as residual water may affect the vapor measurement if collected on the sorbent tubes.

7.3 Complete the required reporting for this section.

7.4 The coupon treatment process is considered complete once the surface of interest has dried or the 30-minute dry time has elapsed. The vapor test time is initiated. (Figure 7A-4).

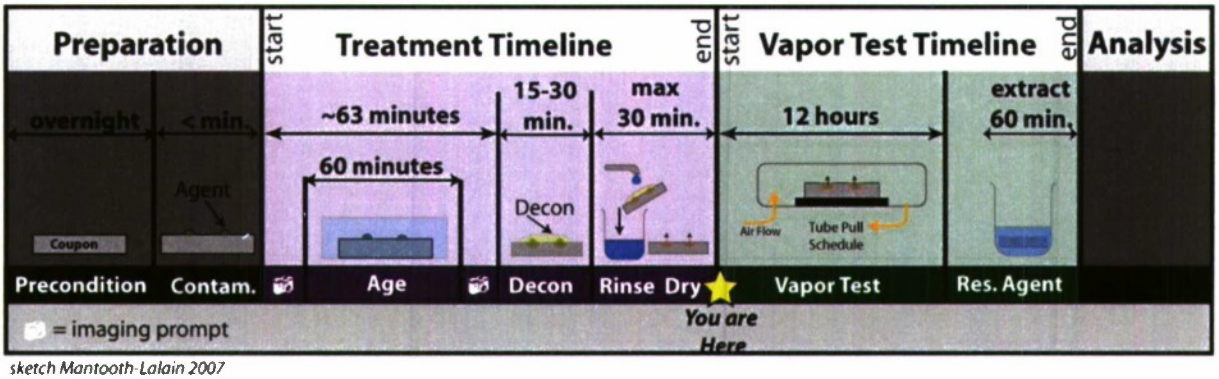

Figure 7A-4. Vapor Test Timeline Representation for Option A.

8.0 Vapor Test

8.1 Place coupon in vapor chamber
8.2 Chamber is sealed
8.3 Air flow is initiated to appropriate experimental settings including chamber and sampling air flow, temperature and relative humidity.
8.4 Vapor collection = time zero
8.5 Collect tubes per vapor sampling plan

9.0 Residual Agent Test

9.1 After the last tube has been collected, the coupon will be extracted for residual agent.

9.1.1 Place the coupon in an extraction jar. For most materials the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

9.1.2 Add 20.0 mL of extraction solvent ensuring coupon is completely immersed.

9.1.3 Place PTFE/ Teflon-lined lid on extraction jar.

9.1.4 Swirl jar.

9.1.5 Coupon will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Procedure 7-D must use the same extraction time.

9.1.6 At the end of the coupon extraction period, swirl jar, open vial and using a clean pipette tip place a sample into an analytical vial for analysis.

9.2 Complete the required reporting for this section.

10.0 Chromatographic analysis for agent

10.1 Samples are analyzed based on guidance in Procedures 7-F and 7-G. This test generates three types of samples for analysis.

- Dose confirmation.
- Vapor tube
- Coupon extract for residual agent.

10.2 Sample dilution may be required for sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

10.3 Obtain list of analytical results for extracts in ng/mL which already accounts any additional dilutions and for sorbent tubes in ng/tube.

10.4 Complete the required reporting for this section.

11.0 Perform Calculations

11.1 Obtain the analytical results for

- Dose confirmation
- Vapor tube
- Coupon extract for residual agent

11.2 Perform calculations.

11.3 Complete the required reporting for this section.

CALCULATIONS – Vapor Sorbent Tubes

Report the mass of contaminant collected on each sorbent tube.

CALCULATIONS – Extract Samples

1.0 Convert Results from ng/mL to ng

1.1 Obtain the chromatography data in ng/mL for the coupon extract (**RE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.

1.2 Convert the residual agent test result from mass in solution (**RE_E**) to mass (**RE_M**)

For each coupon extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{RE_M} \text{ (in ng)} = \mathbf{RE_E} \times \mathbf{EV} \qquad (1)$$

1.3 Calculate 'Analyte Mass Delivered' ***Del*** from dose confirmation sample

For each dose confirmation sample extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

1.4 Average results for replicates reporting standard deviation.

2.0 Calculate the residual agent results corrected for extraction efficiency

2.1 Obtain the calibration curve developed from Procedure 7-D.

2.2 Calculate the extraction efficiency corrected residual agent test result (**RE_C**) in nanograms using the equation identified in step 4.0 of procedure 7-D.

2.3 Report test results.

3.0 Complete the required reporting for this section

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Decontaminants:** Provide for each decontaminant used the decontaminant name / description, source, date of preparation, purchase or expiration date (as applicable). Include a description of the preparation process for materials requiring pre-use preparation such as dilution or mixing.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.
- **Water:** Provide a description of the water used and source for each use of water. For example, laboratory distilled water may have been used to mix the decontaminant and certified ocean seawater might have been used for the rinse. The water reporting would include the description for both the decontaminant prepared and rinse waters used. Include characterization data / specification sheet details for any certified or specialty water used.

EQUIPMENT

- **Contaminant Delivery Tool**
  - Tool identification including manufacturer, model number, and volume dispensing range.
  - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).

- Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
  - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Decontaminant Delivery Tool**
  - *See contaminant delivery tool listing for pipettes and syringes.*
  - For breadboard, brassboard, and prototype equipment, provide a description of the decontamination system including configuration and identification number / name.
  - For vendor provided equipment, provide the vendor name, item description, and model number.
- **Water Rinse Delivery Tool:** *see contaminant delivery tool listing.*
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Environmental Chamber:** Provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems. If a data logger is used, then include the data logging frequency.
- **Vapor Chamber:** provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems.
- **Contaminated Area Measurement (if performed)**: include tool identification including manufacturer and model number, camera resolution, description of area measurement calculation and associated error with calculation if known.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Sorbent Tubes:** include the source, description, part number, and sorbent.
- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, explanation how process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

<u>TEST SPECIFIC</u>: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Precondition Coupons**
  - Option used (A, B or C)
    - For Option C: a description of how the conditioning was performed.
  - Precondition length of time with units of hours and minutes.
  - Temperature average with standard deviation, high, and low for conditioning period.

  - Relative humidity average with standard deviation, high, and low for conditioning period.
  - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.

- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (µL) per coupon.
  - Agent drop volume size(s) in microliters (µL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.

- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (µL) per vial, the agent drop volume size(s) in microliters (µL) per vial, the solvent identification, and the solvent volume.

- **Post-Contamination Surface Contamination Observation**
  - Option used (A, B or C)
  - Written description of applied drops as they appear for each coupon (e.g., sessile, spread).
  - For Option B: how contrasting was achieved.
  - For Option A/B: provide a representative photograph
  - For Option A/B: provide the calculated contaminated surface area
  - For Option C: provide a hand drawing of the representative contaminated area, estimated contaminated surface area, and the method for estimating contaminated surface area.

- **Aging**
  - Option used (A, B or C)
    - For Option C: a description of how the aging was performed.
  - Coupon cover description including source, part number, size, and volume.
  - Aging length of time in units of minutes.
  - Temperature average with standard deviation, high, and low for aging period.
  - Relative humidity average with standard deviation, high, and low for aging period.
  - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.

- **Post-Aging Surface Contamination Observation:** *see requirements for Post-Contamination Surface Contamination Observation.*

- **Pre-Rinse**
  - Option used (A, B or C)
    - For Option C: a description of how rinsing was performed.
  - Rinse material identification (i.e., distilled water, hot soapy tap water, etc.).
  - Rinse material temperature
  - Test location temperature and relative humidity during rinsing.
  - Total volume applied
  - Description of the force and rate rinse applied

- **Decontamination**
  - Option used (A, B or C)

        - For Option C: a description of the decontamination process.
    - Description of the decontaminant application process.
    - Decontaminant temperature.
    - If decontaminant is applied "cold" or "warm" provide a description of how decontaminant was chilled or warmed.
    - Record amount of decontaminant applied
        - For liquids, volume delivered
        - For solids, mass delivered
        - For vapors, injection rate, flow rate, fumigant concentration, temperature, and relative humidity
        - Or other specifications per manufacturer's delivery instructions.
    - Coupon cover description including source, part number, size, and volume.
    - Decontaminant residence time on coupon surface in minutes.
    - Temperature average with standard deviation, high and low for the decontamination period.
    - Relative humidity average with standard deviation, high and low for the decontamination period.

- **Post-Rinse:** see *requirements for Pre-Rinse.*
- **Drying**
    - Option used (A, B or C)
        - For Options A, B and C: a description of how drying was performed.
        - For Option C: if no drying was used, provide a detailed description of how wet the surface was (representative photograph recommended).
    - Drying time in minutes
    - Description of drying location
        - If hood, specify air velocity
        - If flow chamber, specify flow rate and air temperature.
    - Temperature
    - Relative humidity
    - Description of any residual water on surface at the end of the drying period.
    - Detailed description of drying process used.
- **Vapor Test:** include the temperature and relative humidity of vapor chamber, volume of vapor chamber (m^3), chamber air flow rate (mL/min.), sampling air flow rate (mL/min.), sampling time per tube (min.), midpoint time for each sample (min.), mass of analyte on tube for each sample (ng) and confirmation statement that pull times used do not exceed time determined in breakthrough test.
- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the vapor sorbent tube results in nanograms, "dose confirmation" sample mass in nanograms and residual agent coupon results in nanograms per coupon.
- **Calculation Reporting Criteria**
    - Summary data table listing the vapor sorbent tube results. The calculation section must be used to complete test and necessary reporting criteria are included in that section.
    - Summary data table for extract samples containing the following information. Some data may not be available based on Procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
        - Data in nanograms per milliliter (ng/mL) for the residual agent extract (**RE$_E$**) and the dose-confirmation samples (**DC$_E$**) that has been corrected for any dilutions performed between sample collection and analysis.

    - Residual agent mass results (**RE$_M$**), not corrected for extraction efficiency in nanograms.
    - Delivered mass results (***Del***) in nanograms.
    - Extraction efficiency corrected residual agent mass results (**RE$_C$**) in nanograms.
    - Test set (combination of test replicates) averages and standard deviations for data sets specific to reporting results for test objective(s).
  - Summary of the coupon extraction efficiency determination (Procedure 7-D) for each agent – material - extraction solvent combination if Procedure 7-D was not directly executed and reported for this test report.
    - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
  - Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly

variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the amount of contaminant delivered in order to determine the difference. The amount of contaminant delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Aging Temperature and Relative Humidity: Core test moderate condition is 21 ± 3 °C, preferred, ± 5 °C maximum. Aging temperature in general is target temperature ± 5 °C. No criterion for RH is specified, however, a test sponsor may specify depending on test objective.

- Rationale: Changes in temperature directly affect the amount of contaminant absorbed into a material. Any deviation in temperature increases the amount of error in the end test result. Therefore, deviations in temperature must be minimized. For example, mass transport coefficients typically double for every 10 °C increase in temperature.
- Rationale: Relative humidity is expected to have a minor influence on test results compared to other system variables.

Aging Time: Core test aging time is 60 ± 3 min. For other aging times, the acceptance criterion is target time ± 5%.

- Rationale: The more or less time a contaminated coupon is aged, the more or less contaminant is absorbed into the coupon. For example, mass adsorbed for sorptive non-porous materials (based on Fick's first law) is proportional to square root of the aging time. A 5% time deviation could result in a 2.5% variation in mass absorbed into the coupon.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Amount of Decontaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered. In the event these criteria were not met, a repeatability study could be performed to determine the precision of the tool.

Decontaminant Residence Time: The total decontaminant residence time should be within ± 5% target time.

- Rationale: The measurement of the effect the decontaminant has for contaminant reduction is the main objective of the test. The decontaminant–contaminant interaction time will be proportional to the amount of agent removed and or neutralized, likely in a nonlinear manner.

Contaminated Surface Area (Vapor): The contaminated surface area for a test set should be measured as accurately as possible. Prior to collecting data the lowest resolution which can be graphically resolved should be determined and documented. The camera should be calibrated to determine areas (e.g., cm^2/pixel).

- Rationale: This value is used in the data analysis calculations, to determine loading factors.

Vapor Sampling:
The tube sampling time should be < ± 2% of target tube sampling time, with ± 5% maximum

- Rationale: Tube sampling time should be as accurate as possible since this time is directly proportional to agent mass on tube and the sampled air volume. Any inaccuracy in actual tube sampling time will result in under/over estimation of chamber vapor concentration and emission factors.

The tube sampling flow rate should be within ± 5% of the target flow rate.

- Rationale: The tube sampling flow rate should be as accurate as possible. Tube sampling flow rate directly contributes to the sampled air volume. Any inaccuracy in the tube flow rate will result in under/over estimation of the chamber vapor concentration and emission factors.

The acceptance of a reported "below detection" vapor concentration should be carefully evaluated. For situations where low concentrations are expected, the sampling time should be as long as reasonable.

- Rationale: A below detection vapor concentration is dependent on the analytical detection limits and how the sample was collected. Low vapor concentrations sampled for short periods of time may mislead the analyst to conclude that the vapor concentration is zero, it is less than the LOD divided by sampled volume, but may not be zero. This may lead to underestimating the emission factor and ultimately the hazard.

Prior to test, the safe sampling volume specific for the solid sorbent type and agent tested should be determined.

- Rationale: Samples collected in excess of the safe sample volume are likely exhibit breakthrough resulting in an underestimate of the vapor concentration and ultimately result in underestimating the hazard.

The free air volume of the chamber should be known as best as possible. The recommendation is that the volume is known within ± 10%.

- Rationale: The chamber free air volume is used to calculate the loading factor and air change rates. Error in the chamber volume will induce scatter in the emission factor calculations. It is recognized that this may be difficult to physically measure or calculate.

Vapor Emission Model: The vapor emission model should provide a best fit to the data. Though some materials may provide a significant distribution of results, it is recommended that an average RPD value for a model is <15%. However, it is recognized that some materials may never meet this criteria. In all cases, the average RPD value should be reported.

- Note: it is not safe to time extrapolate vapor emission models beyond the last sampled time.

REVISION HISTORY

March 2008: original document in source document format. Based on TOP 8-2-061, 2002 initial release.

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Test Procedure 7-B: Rinsate Analysis for Agent Test Method

SUMMARY OF PROCEDURE

The rinsate analysis method is the measurement of the amount of agent physically removed from the coupon during the decontamination process.

This method is anticipated to be part of the FY08 release.

REVISION HISTORY

March 2008: this is a new method slated for development in the FY08 program.

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Test Procedure 7-C: Baseline Vapor Test Method

SUMMARY OF PROCEDURE

The baseline vapor test method is a complementary procedure to the Laboratory-Scale Decontaminant Performance Evaluation for Vapor Test Method serving as either a positive- (contaminant, no decontaminant) or negative- (no contaminant, decontaminant) control. The most common use is a positive control test to measure the vapor and residual agent when decontaminant is not used. It should not be assumed that the positive control test will result in measurable agent. A reduction in agent compared to the starting challenge may be observed in the test results as a result of agent loss during the decontamination process due to weathering / evaporation. The negative control test is used without contaminant to determine the impact the decontaminant has on the process. For example, aggressive decontaminants may impart impurities into the test materials that may interfere with analytical detection. The positive and negative control baseline tests are identified as Option 1 and Option 2, respectively. This test procedure is conducted using the selected parameters from test Procedure 7-A. This method can be used to evaluate decontaminant performance against liquid-phase contaminants such as chemical-warfare agents, chemical-warfare agent simulants, toxic-industrial-chemicals and toxic-industrial-materials. The terms contaminant and agent are used interchangeably.

This procedure provides the following information:

- **The mass of agent in nanograms recovered from the solid sorbent tube after the decontamination process**.
- **The mass of agent in nanograms recovered from the coupon after the decontamination process and vapor test**

The following prerequisite tests are required for this test procedure:

- Procedure 7-D, "Panel (Coupon) Extraction Efficiency Test Method" is the method for determining the efficiency the selected solvent has for recovering agent from the coupon.
- Procedure 7-H, "Chromatographic Analysis Guidance is the guidance protocol for the analytical analysis of the extracts generated in this test.

This procedure alone does not provide the complete assessment of the decontaminant's performance for reducing the agent contamination or reporting the hazard. The complete assessment of a decontaminant performance should also address:

- The amount of agent physically removed from the coupon during the decontamination process using either liquid decontaminants or post-decontamination rinsing step.
    - Procedure 7-B, "Rinsate Analysis for Agent Test Method" is the measurement of the amount of agent physically removed from the coupon during the decontamination process.
- Reporting the vapor hazard value in mg/m^3.
    - Procedure 7-E, "Data Calculation Method to Report Vapor Hazard" is the process for converting the mass of agent recovered from the sorbent tubes to a reported hazard value.

Limitations and other test variations:

- The collection of vapor data is not a direct measure for percent efficacy, percent neutralization, or reduction in starting challenge. These measurements must be conducted using the appropriate procedures in Chapter 6.
- **Contaminant Simulant:** chemical compounds for chemical agents are often used during early screening or at non-chemical agent surety facilities. A chemical agent simulant is a chemical compound of lower toxicity than the chemical agent with at least one property in similarity to the chemical agent such as certain bonding, functional group, physical property, etc. Simulants should be selected based on the main property being tested for most accurate comparison. Since simulants do not contain all of the same physical and chemical properties of the live agent; simulant data alone is not sufficient to determine decontaminant performance. It is recommended that the simulant performance be confirmed with agent data.
- Bagging and sampling is not an appropriate method to determine a vapor hazard. Bag and sample methods can give an indication if offgassing may be present but due to uncharacterized air flow and uncontrolled volume the measurement cannot provide an accurate assessment of hazard.
- Certain variations fall outside the scope of the Laboratory-Scale Performance Evaluation test methods. This vapor test is directly applicable items that can be placed in appropriate vapor chambers. However, the residual agent measurement is only directly applicable to panels, items or other test surfaces that can be extracted in solvent.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA), in this case the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample**: liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **breadboard, brassboard, prototype** – technology in differing degrees of configuration still under development that is not in final form. This can apply to test fixtures, formulations and/or the decontamination system / applicator.
- **chemical agent** - is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contaminant -** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical and toxic industrial materials. A list of contaminants is provided in Appendix B.

- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in. diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant -** for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process** - The process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically for these procedures, the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing and drying.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – a sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency -** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **hazard -** A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*

- **moderate condition** - test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **nonsorptive materials**: a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **operational decontamination** – decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material and/or working areas, in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate** - the collected rinse from the decontamination process. The sample may include residual decontaminant, agent, or agent byproducts in water.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface, if the droplet significantly spreads across the surface it is better described as a thin film.
- **sorptive or porous materials**: a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition** - for a specific agent – material- decontaminant set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **vapor chamber** – a dynamic vapor microchamber that fully encloses a coupon to enable vapor emission analysis. The chamber must facilitate the ability to control air flow and mixing, collect vapor samples, and measure environmental conditions such as temperature and relative humidity.
- **vapor cell** – a dynamic vapor enclosure that is placed over the surface to be tested for vapor emission analysis. The tested surface serves as one of the 'walls' of the enclosure. The use of a vapor cell is not within the methods described here.

- **vapor hazard** – a value specified in requirements documents usually specified as a concentration (mg/m^3) that should have an accompanying exposure time. The value corresponds to an exposure that presents an acceptable risk level for to unprotected personnel exposed to the vapor concentration. The toxic load model should be applied to calculate a vapor hazard.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Headquarters, Department of the Army (DA), Washington, DC, Field Manual (FM) 3-11.9, Potential Military Chemical/Biological Agents and Compounds, 10 January 2005.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
    - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
    - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
    - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Decontaminants:** The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid- or vapor-phase and may contain a reactive functionality for neutralizing chemical contaminants. A general listing of chemical decontaminants is provided in Appendix B.
- **Extraction solvents:** The residual agent test requires the extraction of agent sorbed into the coupon during testing. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride and solvent blends.
- **Water:** Decontamination processes typically involve a post-rinse step and some decontaminants are made using water. Laboratory testing will use distilled or deionized water unless otherwise instructed by the test sponsor.

EQUIPMENT

The equipment required for this method includes the tools for delivering contaminant, decontaminant and rinse water; maintaining environmental control and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (µL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 µL delivered as two 1 µL drops for a 1 g/m^2 starting challenge.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred to prevent cross-contamination if the tool is used for multiple procedure steps, dosing solutions or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. Also best suited for pipetting volatile liquids. Smallest delivery volume, based on survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
    - Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. Smallest delivery volume based on survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.
    - Computerized Dispensing System: Automated tool with ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.
- **Decontaminant Delivery Tool:** the tool used to deliver a specific volume of decontaminant to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The core coupon test specifies using a decontaminant volume of 1.00 mL. The specific decontaminant under evaluation may use other delivery volumes.

- Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of decontaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
- Spray Bottle: Some applications will mimic a spray application using a spray bottle. The tool should be evaluated to determine the number of pumping actions required to achieve target decontaminant application. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- Developmental Breadboard, Brassboard or Protoype Technology: These are technologies under development that are not in final configuration. The decontaminant generation and delivery may not be known. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.
- Vendor Provided Technology: This is equipment provided from vendor that may be breadboard, brassboard, prototype or commercial in configuration. The technology is operated per vendor guidance. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Water Rinse Delivery Tool:** Tool for the delivery of specific volumes of water to the coupon surface to remove decontaminant from the surface. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. Recommended that tool used has ability to control flow rate to reduce operator-to-operator variations. The typical delivery volume for a 2 in. diameter circular contamination area range is 60 mL.
  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. An example is the Dispensette and Brinkman brands. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
  - Pump: Other precision liquid dispensing systems. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test. Tools obtained or developed by the testing laboratory which has no performance specification standard or vendor provided performance information should be tested to determine their accuracy and precision. At a minimum, the tool should be used reproducibly from test-to-test and the exact usage should be documented.

- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.
    - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.
- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.
    - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.
    - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.
- **Environmental Chamber:** Temperature and relative humidity controlled chamber for the preconditioning and aging coupons. The fixture should be able to maintain test specific environmental conditions (e.g., temperature and relative humidity) even when adding or removing samples. The system must have temperature and relative humidity data logger capability, be able to store and download temperature and humidity data and traces to a computer for further analysis. System must be able to maintain temperature and relative humidity. System operation and range should be known.
- **Contaminated Area Measurement:** Fixed-site photographic setup to visually capture the agent contamination surface area coverage after dosing, aging and any other critical steps in the decontamination process. Photograph resolution of 9 to 25 pixels per droplet measured is recommended for surface area calculations.
    - Digital Camera on Fixed Stand
    - Imaging Station
- **Vapor Chamber:** An enclosed structure of sufficient size that completely contains the coupon/test article with the following requirements. General guidance for vapor chamber construction can be located in ASTM D 5116-06 “Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.” Several considerations for decontaminant evaluations are provided in the bulleted list.
    - The chamber should be constructed of inert materials.

  - The chamber should ideally run under positive pressure to minimize contamination inside the chamber.
  - The vapor chamber must have a clean air supply with tight control of the chamber air flow rate (±5% minimum).
    - Mass flow controllers or mass flow meters are preferred over volumetric flow meters (requires standard temperature and pressure (STP) correction).
  - The chamber should have the ability to measure temperature and humidity, control of temperature and humidity are ideal.
  - The chamber should provide a well mixed environment.
  - The volume of the chamber must be known.
  - The chamber must have an exhaust port to enable collection of vapor samples.
  - The sampling air flow must be known.
- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Procedures 7-F and 7-G. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used/

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the coupon. A glass container such as a vial or jar of sufficient size to hold both the coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommended for chemical agent testing.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** are typically used during the aging step to cover the coupon surface to minimize evaporative loss. Can also be used as sample holder.
- **Rinsate collection container:** If rinse water analysis is required, the rinse should be collected in a glass container of sufficient volume for the rinse water and extraction solvent, preferably a wide mouth jar. It is recommended to limit use of funnels or other tools that may uptake agent during collection. Use of plastic containers is not

recommended for chemical agent testing. The container cap should be inert lined to prevent extraction of plasticizers or other impurities into the sample.

- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **Transfer pipettes**
- **Timing device(s):** Test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Solid sorbent tubes:** a tube such as a depo area air monitoring (DAAM) tube that contains a solid sorbent that absorbs the contaminant. Typical solid sorbents include Tenax, Chromasorb or Haysep. The appropriate sorbent should be used for the contaminant being tested. ASTM method D 6196 "Practice for Selection of Sorbents, Sampling, and Thermal Desorption analysis Procedures for Volatile Organic Compounds in Air" provides detailed guidance for the selection of the appropriate sorbent tube.
- **Optional items:** Items that may be used based on test sponsor or vendor decontaminant include vapor generators, spray bottles, analytical balance, stir plate, stir bars, vortexer, pH meter

SAFETY PRECAUTIONS

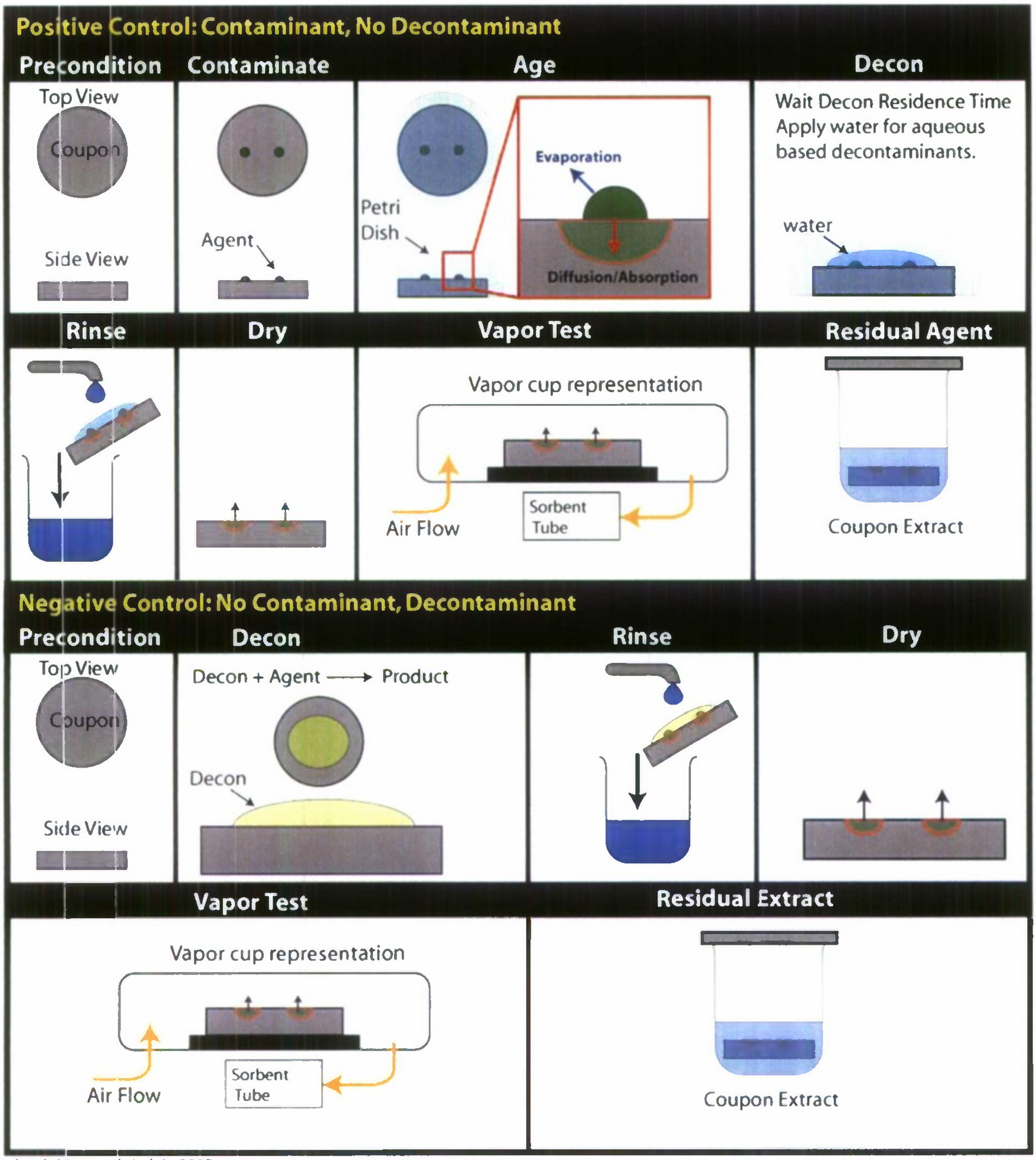
This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between engineering controls / hoods), sample decontamination and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements.

This test has Options 1 and 2 for the positive- (contaminant, no decontaminant) or negative- (no contaminant, decontaminant) control, respectively. This test aligns with test Method 7-A requiring the use of the identical test process used. Test Procedure 7-A has Options A, B and C that are step variations based on potential variables that could be explored. The core test evaluation is designated by Option A. This option is based on a liquid decontaminant tested at moderate environmental conditions using equipment with known accuracy. This option should be used unless otherwise instructed by a test sponsor. Option B is similar to Option A but allows for different parameters, such as temperature. Option C is designed for the evaluation of new technologies or the use of conditions outside of the core test. The use of lettering does not indicate a test grade. The letter serves as a quick reference to the selections made during testing and the considerations required for comparing different groups of data. Option A and B

parameter choices are preferred in cases where lab-data must be compared to requirements; however, Option C parameters may need to be used, especially for the evaluation of new technologies.



sketch Mantooth-Lalain 2007

Figure 7C-1. Positive and Negative Control Test Sketch for Vapor.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- **Identify the calculation desired. Review the Calculation Procedure 7-E and select appropriate test methods and options within a test method to ensure the necessary data is collected.**
- Turning on equipment that will need to thermally equilibrate (i.e., environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars) and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Prepare decontaminant.
- Decontaminant preparation.
- Obtaining the Procedure 7-A process to be used.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- It is recommended that contaminant equilibrate to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination, and rinse test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of five coupons per test condition and three dose-confirmation samples per contamination set.

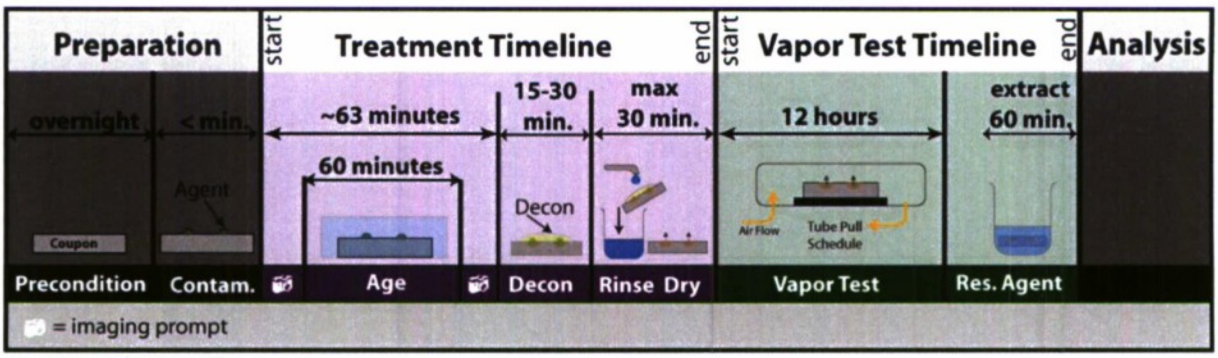


Figure 7C-2. Vapor Test Timeline Representation for Procedure 7-A Option A.

Note: Reproduction of this sketch must carry sketch credit to Mantooth-Lalain.

2.0 Precondition Coupons

2.1 Set the environmental chamber to the specified test condition

METHOD 7–A OPTIONS:

OPTION A (core test): moderate condition test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported.

OPTION B (core test, variable condition): variable condition test with environmental chamber using test sponsor / director temperature and relative humidity set-point. Most common test cases are high and low temperature and relative humidity.

OPTION C (outside core test): test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupon conditioning is to occur using the same method including temperature, relative humidity, location and time as that used in Procedure 7-A .

OPTION 2 - Negative Control (no contaminant, decontaminant): the coupon conditioning is to occur using the same method including temperature, relative humidity, location and time as that used in Procedure 7-A .

2.2 Allow environmental chamber to equilibrate at the set-point temperature and relative humidity. The time to reach set-point equilibration may vary based on equipment and set-point conditions. Recommended that temperature and humidity are maintained at the set-point for at least 30 min prior to the start of conditioning.

2.3 The coupons are placed horizontally on coupon trays with the test surface to be contaminated / decontaminated facing upwards.

2.4 Once the chamber has equilibrated at the set-point temperature and relative humidity, place the trays into the environmental chamber for at least 60 min. Recommended practice if possible is to precondition the test materials overnight.

- Note: some materials may require special preconditioning treatments. For example, cellulose based materials and concrete contain significant moisture. These types of materials do not typically achieve moisture equilibrium in less than 24 to 48 hours. Longer precondition times may be required for certain materials. An example procedure for wood is ASTM D4442.

2.5 Samples should not be removed until ready to execute Step 3 Contaminate Coupons.

2.6 Complete the required reporting for this section.

3.0 Contaminate Coupons

3.1 Identify contamination density to include number of drops, drop volume and deposition pattern.

METHOD 7–A OPTIONS:

OPTION A (core test): contamination density is 1-1.2 g/m^2 applied using pipette / syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): variable contamination density is typically between 1 to 10 g/m^2 applied using pipette / syringe or equivalent tool as variable sized drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

OPTION C (outside core test): application of agent using brushes, rollers or sprays applicators such that the amount of agent applied to the specific surface is not tightly

quantifiable. Note: calculation of percent neutralization might not be feasible using this option.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupon contamination is to occur using the identical process used for the Procedure 7-A testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied.

3.2 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with clean, appropriate pipette tip

3.4 Load contaminant delivery tool in accordance with manufacture's directions.

3.5 Deliver to the surface the appropriate number of drops to achieve the contamination density. Reload the tool and repeat as needed for total number of coupons. Treatment time starts after coupon is contaminated. Recommended use of timing charts for multiple samples.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests) or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.6 If using pipettes or syringes to deliver contaminant, prepare the "dose confirmation" sample. Recommend at least three replicate samples.

3.6.1 Delivering to a scintillation vial the appropriate number of drops to achieve the contamination density.

3.6.2 Add 20 mL of extraction solvent.

3.6.3 Cap vial

3.6.4 Thoroughly mix contents by inverting vial three times.

3.6.5 Using a clean, disposable pipette load the analytical vial with aliquot of extractant solution.

3.7 Observe the post-contamination drop interaction with the surface and surface coverage.

METHOD 7–A OPTIONS:

OPTION A (core test): using digital camera or imaging station, photograph each coupon surface.

OPTION B (core test variable condition): some materials may not allow for the rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three independent coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered documented both in words and hand drawing.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical process used for the Procedure 7-A testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied, skip to step 5.

3.8 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

3.9 Complete the required reporting for this section.

4.0 Coupon Aging

4.1 Coupons are aged.

METHOD 7–A OPTIONS:

OPTION A (core test): Coupons are aged in environmental chamber for 60 min at moderate condition test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported. Environmental chamber should have logging capability for real-time temperature and humidity recording.

OPTION B (core test, variable condition): Coupons are aged in environmental chamber under one or more of the following cases. The environmental chamber should have logging capability for real-time temperature and humidity recording.

- Variable temperature and relative humidity: aging conducted at test sponsor / director designated temperature and relative humidity.
- Variable aging time: shorter aging time for immediate or operational decontaminant applications, or aging period longer than the Option A basic thorough test. The aging may be at the moderate condition and/or variable temperature and relative humidity.

OPTION C (outside core test): test is conducted at room condition without the use of an environmental chamber. Note room condition is the temperature at the test location on a given test day. This could be warm, moderate or cold.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the coupons are aged using the identical procedure as the Procedure 7-A testing.

OPTION 2 - Negative Control (no contaminant, decontaminant): skip to step 5.

4.2 Observe the post-aging drop interaction with the surface and surface coverage. (If no aging period is used, this step can be skipped).

METHOD 7–A OPTIONS:

OPTION A (core test): using digital camera or imaging station, photograph each coupon surface. There is a chance for some materials the post aging image may not be visible without use of color indicator or dye.

OPTION B (core test variable condition): some materials may not allow for the rigorous photography without the use of a color dye for contrast enhancement. In such cases, a minimum of three coupon replicates should be carried through the test process and treated to enable digital photography.

OPTION C (outside core test): If digital photography cannot be conducted, the drop surface interaction and estimated percent surface area covered documented both in words and hand drawing.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical process used for the Procedure 7-A testing should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): contaminant is not applied.

4.3 Complete the required reporting for this section.

4.4 Coupons are moved to decontamination test area at end of aging period.

5.0 Pre-rinse the Coupons

5.1 Coupons are rinsed.

METHOD 7–A OPTIONS:

OPTION A (core test): pre-rinse is not used for the core test.

OPTION B (core test variable condition): Pre-rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for process and analysis under Procedure 7-B. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION C (outside core test): the use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 7-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 7-A should be used here.

5.2 Complete the required reporting for this section.

6.0 Decontaminate the Coupons

6.1 Apply decontaminant

METHOD 7–A OPTIONS:

OPTION A (core test): For the core test there are a few sub-options based on the test objective. The decontaminants are liquid-phase and applied using a pipette. Dispensettes or pumps may fall under Option A if the decontaminant delivery volume to the contaminated region can be accurately measured. Unless otherwise specified, the decontaminant applied is typically at room conditions. The amount of decontaminant applied is based on the following guidance.

- Option A-1: For early research tests, it is recommended that 1.00 mL of decontaminant is evenly dispensed over the contaminated coupon surface in a single application. Care should be taken to ensure that the decontaminant is delivered uniformly over the test area. This recommended decontaminant volume is for starting challenges in the 1 to 10 g/m^2 range to ensure that decontaminant covers the contaminated surface area. Some agent-material interactions could result in significant contaminated surface coverage that smaller decontaminant volumes may not be able to adequately cover the entire contaminated surface yielding data scatter due to decontaminant delivery.
- Option A-2: FM 3-11.5 recommends a decontaminant to contaminant ratio of 50:1. This corresponds to 0.100 mL to 1.000 mL for a 1 to 10 g/m^2 starting challenge, respectively.

OPTION B (core test variable condition): Some liquid-phase decontaminants may require applying more or less decontaminant. For vapor-phase decontaminants apply appropriate fumigant concentration.

OPTION C (outside core test): the use of solid decontaminants, sorbent wipes, brushing or mechanical scrubbing methods are outside the scope. These materials have the potential to retain or physically relocate agent. The use of these methods requires adjustment to calculating percent neutralization. Breadboard, Brassboard, Prototype or vendor provided equipment with specified application processes falls here, decontaminant is applied as best as possible in accordance with technology operating procedures.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): decontaminant is not applied.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 7-A should be used here

6.2 Cover coupons with Petri dish (or equivalent) cover to minimize cross contamination and evaporative loss.

6.3 Wait appropriate decontaminant residence time at specified environmental condition

METHOD 7–A OPTIONS:

OPTION A (core test): standard decontaminant residence time is from 15 to 30 min for liquid-phase decontaminants in environmental chamber at ambient condition test using environmental chamber set to 21 ± 3 °C (70 ± 5 °F) preferred, with ± 5 °C maximum. Temperature spans greater than ± 5 °C may introduce significant scatter. Relative humidity should be measured and reported. Environmental chamber should have charting capability for real-time temperature and humidity logging.

OPTION B (core test variable condition): liquid-phase decontaminants outside the 15- to 30-minute range or at variable temperature or humidity that are placed in environmental chamber for residence period.

OPTION C (outside core test): liquid phase decontaminants evaluated at room condition. Sorbents and wipes may have other residence times on surface. Vapor-phase decontaminants may dictate environmental conditions as part of process. Breadboard, Brassboard, Prototype or vendor provided equipment with specified application processes using residence times outside the core 15 to 30 min or environmental conditions outside specified test conditions fall here.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): The baseline study uses the identical procedure from Procedure 7-A. The identical decontaminant residence time, temperature and relative humidity should be use. If the decontaminant process utilizes

air movement (i.e., vaporous decontaminants), the identical process parameters and decontaminant residence time are used.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 7-A should be used here.

6.4 Complete the required reporting for this section.

7.0 Post-Rinse and Dry

7.1 Coupons are rinsed.

METHOD 7–A OPTIONS:

OPTION A (core test): Rinse is applied by delivering 60 mL of room temperature water to the coupon. Rinse water is collected in glass jar for process and analysis under Procedure 7-B. Coupons may be rinsed by either of the following procedures:

- If coupons are individually handled, all surfaces should be rinsed (i.e., front and back). The preferred rinsing pattern is three 20 mL aliquots applied to the front, front and back.
- If coupons are situated in a flow-through fixture, 60 mL is applied to the contaminated surface. Care should be taken that minimal liquid is retained in the fixture. If additional water must be applied to rinse the fixture, that water should also be collected and analyzed.

OPTION B (core test variable condition): Rinse is not collected or analyzed.

OPTION C (outside core test): the use of pressure washers fall outside the core test as the process forces can vary enough to affect physical removal amounts. Also, some applicators may not allow for rinse water to be collected for analysis. At this time hot soapy water falls outside the core test as the rinse evaluation method needs to be completed and determine impact of surfactant on accurate agent measurement. Some decontaminants do not require a post rinse. The impact of residual decontaminant on the analytical measurements must be evaluated.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 7-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 7-A should be used here.

7.2 Coupon drying

METHOD 7–A OPTIONS:

OPTION A (core test): Passive drying is recommended at room conditions, preferably in a chemical fume hood (or equivalent) with approximately 100 linear feet per minute (lfm) airflow. The coupons are recommended to be placed at and angle to increase air flow over surface. Coupons should not be dried for more than 30 min. Residual water on surface should be noted. For most applications wicking the last bead of rinse water should have little impact on the results.

OPTION B (core test variable condition): Controlled air drying which is an active blowing with established air temperature, flow rate, etc.

OPTION C (outside core test): Blotting, wiping or other direct surface contact methods that may also remove agent as part of the process. These methods can impact vapor measurement. No drying would also fall here as residual water may affect the vapor measurement if collected on the sorbent tubes.

THIS METHOD OPTIONS:

OPTION 1 – Positive Control (contaminant, no decontaminant): the identical procedure used in Procedure 7-A should be used here.

OPTION 2 - Negative Control (no contaminant, decontaminant): the identical procedure used in Procedure 7-A should be used here.

7.3 Complete the required reporting for this section.

7.4 The coupon treatment process is considered complete once the surface of interest has dried or the 30-minute dry time has elapsed. The vapor test time is initiated. (Figure 7A-3).

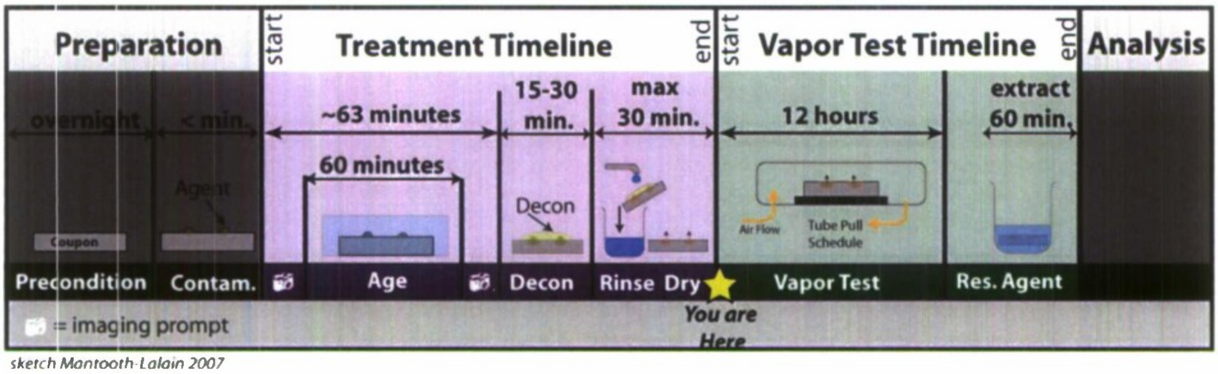


Figure 7A-3. Vapor Test Timeline Representation for Option A.

8.0 Vapor Test

8.1 Place coupon in vapor chamber

8.2 Chamber is sealed

8.3 Air flow is initiated to appropriate experimental settings including chamber and sampling air flow, temperature and relative humidity.

8.4 Vapor collection = time zero

8.5 Collect tubes per vapor sampling plan

9.0 Residual Agent Test

9.1 After the last tube has been collected, the coupon will be extracted for residual agent.

9.1.1 Place the coupon in an extraction jar. For most materials the contaminated side is placed face-up. However, if the material being tested floats, place the sample face-down so that solvent contact occurs.

9.1.2 Add 20.0 mL of extraction solvent ensuring coupon is completely immersed.

9.1.3 Place PTFE/ Teflon-lined lid on extraction jar.

9.1.4 Swirl jar.

9.1.5 Coupon will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction efficiency measured in Procedure 7-D must use the same extraction time.

9.1.6 At the end of the coupon extraction period, swirl jar, open vial and using a clean pipette tip place a sample into an analytical vial for analysis.

9.2 Complete the required reporting for this section.

10.0 Chromatographic analysis for agent

10.1 Samples are analyzed based on guidance in Procedures 7-F and 7-G. This test generates three types of samples for analysis.

- Dose confirmation.
- Vapor tube
- Coupon extract for residual agent.

10.2 Sample dilution may be required for sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

10.3 Obtain list of analytical results for extracts in ng/mL which already accounts any additional dilutions and for sorbent tubes in ng/tube.

10.4 Complete the required reporting for this section.

11.0 Perform Calculations

11.1 Obtain the analytical results for

- Dose confirmation
- Vapor sorbent tube
- Coupon extract for residual agent

11.2 Perform calculations.

11.3 Complete the required reporting for this section.

CALCULATIONS – Vapor Sorbent Tubes

Report the mass of contaminant collected on each sorbent tube.

CALCULATIONS – Extract Samples

1.0 Convert Results from ng/mL to ng

1.1 Obtain the chromatography data in ng/mL for the coupon extract (**RE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.

1.2 Convert the residual agent test result from mass in solution (**RE_E**) to mass (**RE_M**)

For each coupon extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\mathbf{RE_M} \text{ (in ng)} = \mathbf{RE_E} \times \mathbf{EV} \qquad (1)$$

1.3 Calculate 'Analyte Mass Delivered' ***Del*** from dose confirmation sample

For each dose confirmation sample extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\boldsymbol{Del} \text{ (in ng)} = \mathbf{DC_E} \times \mathbf{EV} \qquad (2)$$

1.4 Average results for replicates reporting standard deviation.

2.0 Calculate the residual agent results corrected for extraction efficiency

2.1 Obtain the calibration curve developed from Procedure 7-D.

2.2 Calculate the extraction efficiency corrected residual agent test result ($\mathbf{RE_C}$) in nanograms using the equation identified in step 4.0 of procedure 7-D.

2.3 Report test results.

3.0 Complete the required reporting for this section

TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information**: provide for each contaminant used the contaminant name, source, purity and lot.

- **Decontaminants:** Provide for each decontaminant used the decontaminant name / description, source, date of preparation, purchase or expiration date (as applicable). Include a description of the preparation process for materials requiring pre-use preparation such as dilution or mixing.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.
- **Water:** Provide a description of the water used and source for each use of water. For example, laboratory distilled water may have been used to mix the decontaminant and certified ocean seawater might have been used for the rinse. The water reporting would include the description for both the decontaminant prepared and rinse waters used. Include characterization data / specification sheet details for any certified or specialty water used.

EQUIPMENT

- **Contaminant Delivery Tool**
    - Tool identification including manufacturer, model number, and volume dispensing range.
    - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
    - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
    - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Decontaminant Delivery Tool**
    - *See contaminant delivery tool listing for pipettes and syringes.*
    - For breadboard, brassboard, and prototype equipment, provide a description of the decontamination system including configuration and identification number / name.
    - For vendor provided equipment, provide the vendor name, item description, and model number.
- **Water Rinse Delivery Tool:** *see contaminant delivery tool listing.*
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Environmental Chamber:** Provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems. If a data logger is used, then include the data logging frequency.
- **Vapor Chamber:** provide a description of the chamber including manufacturer and model number for commercial items or a description for fabricated systems.
- **Contaminated Area Measurement (if performed)**: include tool identification including manufacturer and model number, camera resolution, description of area measurement calculation and associated error with calculation if known.
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Sorbent Tubes:** include the source, description, part number, and sorbent.
- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, or explanation of how the process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Precondition Coupons**
  - Option used (A, B or C)
    - For Option C: a description of how the conditioning was performed.
  - Precondition length of time with units of hours and minutes.
  - Temperature average with standard deviation, high, and low for conditioning period.
  - Relative humidity average with standard deviation, high, and low for conditioning period.
  - Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.
- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (μL) per coupon.
  - Agent drop volume size(s) in microliters (μL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Confirmation Sample Preparation:** include the contamination density in g/m^2, the total agent volume in microliters (μL) per vial, the agent drop volume size(s) in microliters (μL) per vial, the solvent identification, and the solvent volume.
- **Post-Contamination Surface Contamination Observation**
  - Option used (A, B or C)
  - Written description of applied drops as they appear for each coupon (e.g., sessile, spread).
  - For Option B: how contrasting was achieved.
  - For Option A/B: provide a representative photograph
  - For Option A/B: provide the calculated contaminated surface area
  - For Option C: provide a hand drawing of the representative contaminated area, estimated contaminated surface area, and the method for estimating contaminated surface area.
- **Aging**
  - Option used (A, B or C)
    - For Option C: a description of how the aging was performed.
  - Coupon cover description including source, part number, size, and volume.
  - Aging length of time in units of minutes.

- Temperature average with standard deviation, high, and low for aging period.
- Relative humidity average with standard deviation, high, and low for aging period.
- Identification and discussion of any temperature or humidity excursions to include excursion value, duration, and suspected cause.

- **Post-Aging Surface Contamination Observation:** *see requirements for Post-Contamination Surface Contamination Observation.*
- **Pre-Rinse**
  - Option used (A, B or C)
    - For Option C: a description of how rinsing was performed.
  - Rinse material identification (i.e., distilled water, hot soapy tap water, etc.).
  - Rinse material temperature
  - Test location temperature and relative humidity during rinsing.
  - Total volume applied
  - Description of the force and rate rinse applied
- **Decontamination**
  - Option used (A, B or C)
    - For Option C: a description of the decontamination process.
  - Description of the decontaminant application process.
  - Decontaminant temperature.
  - If decontaminant is applied "cold" or "warm" provide a description of how decontaminant was chilled or warmed.
  - Record amount of decontaminant applied
    - For liquids, volume delivered
    - For solids, mass delivered
    - For vapors, injection rate, flow rate, fumigant concentration, temperature, and relative humidity
    - Or other specifications per manufacturer's delivery instructions.
  - Coupon cover description including source, part number, size, and volume.
  - Decontaminant residence time on coupon surface in minutes.
  - Temperature average with standard deviation, high and low for the decontamination period.
  - Relative humidity average with standard deviation, high and low for the decontamination period.
- **Post-Rinse:** *see requirements for Pre-Rinse.*

- **Drying**
  - Option used (A, B or C)
    - For Options A, B and C: a description of how drying was performed.
    - For Option C: if no drying was used, provide a detailed description of how wet the surface was (representative photograph recommended).
  - Drying time in minutes
  - Description of drying location
    - If hood, specify air velocity
    - If flow chamber, specify flow rate and air temperature.
  - Temperature
  - Relative humidity
  - Description of any residual water on surface at the end of the drying period.
  - Detailed description of drying process used.
- **Vapor Test:** include the temperature and relative humidity of vapor chamber, volume of vapor chamber (m^3), chamber air flow rate (mL/min.), sampling air flow rate (mL/min.), sampling time per tube (min.), midpoint time for each sample (min.), mass of analyte on tube for each sample

(ng) and confirmation statement that pull times used do not exceed time determined in breakthrough test.

- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the vapor sorbent tube results in nanograms, "dose confirmation" sample mass in nanograms and residual agent coupon results in nanograms per coupon.
- **Calculation Reporting Criteria**
    - Summary data table listing the vapor sorbent tube results. The calculation section must be used to complete test and necessary reporting criteria are included in that section.
    - Summary data table for extract samples containing the following information. Some data may not be available based on Procedure selections. Calculations that cannot be performed (e.g., extraction efficiency correction) should be clearly noted in the test report.
        - Data in nanograms per milliliter (ng/mL) for the residual agent extract (**RE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
        - Residual agent mass results (**RE_M**), not corrected for extraction efficiency in nanograms.
        - Delivered mass results (***Del***) in nanograms.
        - Extraction efficiency corrected residual agent mass results (**RE_C**) in nanograms.
        - Test set (combination of test replicates) averages and standard deviations for data sets specific to reporting results for test objective(s).
    - Summary of the coupon extraction efficiency determination (Procedure 7-D) for each agent – material - extraction solvent combination if Procedure 7-D was not directly executed and reported for this test report.
        - Note: it is recommended that this information be generated as an Appendix that can accompany reports as this test is typically performed once per lot of material.
    - Reporting statement: It is recommended that report conclusion statements also capture the key test variables that may affect reported result for full context. The reporting statement should capture the % contaminated surface area, temperature, relative humidity, decontaminant residence time.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of <10%; however testing of specific materials generates reported test errors of >100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

<u>**Recommended Data Acceptance Parameters and Rationale**</u>

Amount of Contaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered.

- Rationale: The percent neutralization, percent efficacy and reduction in starting challenge calculations require knowing the amount of contaminant delivered in order to determine the difference. The amount of contaminant delivered is confirmed through the analysis of the tool characterization samples. The tool characterization samples provide the actual contamination density compensating for agent temperature (altering the density of the agent) and purity differences.

Aging Temperature and Relative Humidity: Core test moderate condition is 21 ± 3 °C, preferred, ± 5 °C maximum. Aging temperature in general is target temperature ± 5 °C. No criterion for RH is specified, however, a test sponsor may specify depending on test objective.

- Rationale: Changes in temperature directly affect the amount of contaminant absorbed into a material. Any deviation in temperature increases the amount of error in the end test result. Therefore, deviations in temperature must be minimized. For example, mass transport coefficients typically double for every 10 °C increase in temperature.
- Rationale: Relative humidity is expected to have a minor influence on test results compared to other system variables.

Aging Time: Core test aging time is 60 ± 3 min. For other aging times, the acceptance criterion is target time ± 5%.

- Rationale: The more or less time a contaminated coupon is aged, the more or less contaminant is absorbed into the coupon. For example, mass adsorbed for sorptive non-porous materials (based on Fick's first law) is proportional to square root of the aging time. A 5% time deviation could result in a 2.5% variation in mass absorbed into the coupon.

Test Event Timing: The time between tasks should not exceed 3 minutes. For other event times, the acceptance criterion is target time ± 5%.

- Rationale: Once a test has begun, event timing is crucial. The time between events should be minimized. Event times that are outside the acceptance criteria will induce error and or bias into the final test results, potentially making the test results unusable especially for regulatory requirement, test-to-test and lab-to-lab comparisons. For example, the longer a contaminated coupon is allowed to age may induce a negative bias. The contact touch duration that is longer than specified will likely induce a positive bias.
- Note: For tests executed at temperatures different than the room condition, the amount of time spent outside of a temperature controlled region may alter the temperature of the test materials, and should be minimized.

Amount of Decontaminant Delivered: Precision dispensing tool (e.g., pipette) calibration should be current and compliant with the required performance specifications listed in the most current versions of the ISO 8655 Parts 1 and 2 or ASTM E 1154 for the volumes being delivered. In the event these criteria were not met, a repeatability study could be performed to determine the precision of the tool.

Decontaminant Residence Time: The total decontaminant residence time should be within ± 5% target time.

- Rationale: The measurement of the effect the decontaminant has for contaminant reduction is the main objective of the test. The decontaminant–contaminant interaction time will be proportional to the amount of agent removed and or neutralized, likely in a nonlinear manner.

Contaminated Surface Area (Vapor): The contaminated surface area for a test set should be measured as accurately as possible. Prior to collecting data the lowest resolution which can be graphically resolved should be determined and documented. The camera should be calibrated to determine areas (e.g., cm^2/pixel).

- Rationale: This value is used in the data analysis calculations, to determine loading factors.

Vapor Sampling:

The tube sampling time should be < ± 2% of target tube sampling time, with ± 5% maximum

- Rationale: Tube sampling time should be as accurate as possible since this time is directly proportional to agent mass on tube and the sampled air volume. Any inaccuracy in actual tube sampling time will result in under/over estimation of chamber vapor concentration and emission factors.

The tube sampling flow rate should be within ± 5% of the target flow rate.

- Rationale: The tube sampling flow rate should be as accurate as possible. Tube sampling flow rate directly contributes to the sampled air volume. Any inaccuracy in the tube flow rate will result in under/over estimation of the chamber vapor concentration and emission factors.

The acceptance of a reported "below detection" vapor concentration should be carefully evaluated. For situations where low concentrations are expected, the sampling time should be as long as reasonable.

- Rationale: A below detection vapor concentration is dependent on the analytical detection limits and how the sample was collected. Low vapor concentrations sampled for short periods of time may mislead the analyst to conclude that the vapor concentration is zero, it is less than the LOD divided by sampled volume, but may not be zero. This may lead to underestimating the emission factor and ultimately the hazard.

Prior to test, the safe sampling volume specific for the solid sorbent type and agent tested should be determined.

- Rationale: Samples collected in excess of the safe sample volume are likely exhibit breakthrough resulting in an underestimate of the vapor concentration and ultimately result in underestimating the hazard.

The free air volume of the chamber should be known as best as possible. The recommendation is that the volume is known within ± 10%.

- Rationale: The chamber free air volume is used to calculate the loading factor and air change rates. Error in the chamber volume will induce scatter in the emission factor calculations. It is recognized that this may be difficult to physically measure or calculate.

Vapor Emission Model: The vapor emission model should provide a best fit to the data. Though some materials may provide a significant distribution of results, it is recommended that an average RPD value for a model is <15%. However, it is recognized that some materials may never meet this criteria. In all cases, the average RPD value should be reported.

- Note: it is not safe to time extrapolate vapor emission models beyond the last sampled time.

REVISION HISTORY

March 2008: original document in source document format. Based on TOP 8-2-061, 2002 initial release.

Test Procedure 7-D: Panel (Coupon) Extraction Efficiency Test Method

SUMMARY OF PROCEDURE

The coupon extraction efficiency test method determines the amount of agent that can be recovered from the coupon using a specific solvent and extraction time. The mass of agent extracted is compared to the mass originally delivered to enable correction of analytical data based on solvent extraction efficiency for a given extraction time. Any loss in the system, such as evaporation, will contribute to lowering the measured extraction efficiency value. The delivered mass (e.g., dose confirmation sample) must be accurately measured to calculate the extraction efficiency. Dose-confirmation samples are used to measure the delivered mass. The test covers a range of concentrations equivalent to 250 mg/m^2 down to requirement levels, which at the time of writing are approximately as low as 0.005 mg/m^2. These results are used to correct the reported residual agent mass values reported in Procedures 7-A and 7-C

This procedure provides the following information:

- An extraction efficiency correction calibration curve for the correction of agent mass reported as a function of the solvent extraction efficiency for a given extraction time.
- This method should be performed when any major changed is made in the laboratory process. Major changes include, new material lot, change in extraction procedure (e.g., time, temperature, extraction volume), change in solvent (e.g., different solvent or change in solvent grade used).

The following prerequisite tests are required for this test procedure:

- Procedure 7-F, "Chromatographic Analysis of Test Extracts Guidance" is the guidance protocol for the analytical analysis of the extracts generated in this test.

Limitations:

- For ultra-low dose levels, non-detect recovery masses may be observed giving the appearance of a low-extraction efficiency. The calculations for determine the extraction efficiency calibration curve account for this situation.
- An assumption of this procedure is that all mass lost is attributed to incomplete extraction. Care should be taken in executing the method to ensure minimal agent loss occurs due to evaporation (especially for more volatile compounds) and coupon handling.
- The extraction efficiency calibration curve should only be used for the contamination drop volume and deposition pattern tested for an agent– material–solvent combination. If other drop volumes, deposition patterns or solvents are routinely used for an agent-material pair, then the extraction efficiency calibration curve should be generated for each drop volume, deposition pattern, agent, material and solvent combination.
- The evaluation of reactive materials can create challenges for extraction efficiency measurements as neutralization may be occurring during the extraction process.

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **absorption** – the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption** – the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **agent** – see chemical agent. Used interchangeably with contaminant.
- **ambient temperature** – the temperature of the surrounding air (EPA), in this case the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample**: liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **chemical agent** - is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **contaminant -** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination -** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant -** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon -** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling** - treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **detection limit** – the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose confirmation sample** – a sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or

reduction in starting challenge that require accurate measurement of the starting contamination.

- **extraction** – the separation of a component from a mixture through selective solubility.
- **extraction efficiency** - the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **limit of detection** – LOD see *detection limit.*
- **limit of quantitation** – LOQ see *quantitation limit.*
- **moderate condition** - test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization** - the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)
- **nonsorptive materials**: a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **panel** – *see coupon.*
- **quantitation limit** – the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **residual agent** - the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **room condition** - the temperature and relative humidity of the test location on the specific test day.
- **sessile drop** – a liquid droplet that is firmly attached to a surface, if the droplet significantly spreads across the surface it is better described as a thin film.
- **sorptive or porous materials**: a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition** - for a specific agent – material- decontaminant set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.

REFERENCED DOCUMENTS

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

REAGENTS, MATERIALS AND EQUIPMENT

REAGENTS

- **Contaminants:** The specific contaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminant evaluation contaminants typically fall into one of three categories.
  - Chemical Agent: Work with chemical agents can only be conducted in approved facilities by specially trained personnel. The types of chemical agents tested include but are not limited to those documented in FM 3-11.9 "Potential Military Chemical/Biological Agents and Compounds."
  - Chemical Agent Simulant: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. Appendix B contains a general listing of commonly used chemical agent simulants.
  - Toxic Industrial Chemicals (TICs) and Materials (TIMs): TICs and TIMs are chemicals produced for industrial applications that are toxic to humans. Testing may include but is not limited to the published listing from "Task Force 25: Hazard from Industrial Chemicals Final Report" dated April 1998 which is summarized in Appendix B.
- **Extraction solvents:** The test requires the extraction of sorbed agent sorbed from test materials such as the coupon. Typical solvents include but are not limited to chloroform, hexane, isopropyl alcohol, methylene chloride and solvent blends.

EQUIPMENT

The equipment required for this method includes tools for delivering contaminant and preparing analytical samples. Several equipment options exist ranging in accuracy and complexity. The appropriate tool should be selected based on the test requirements and acceptable measurement uncertainty. The listed equipment is based on commercial items with known accuracy, precision and/or repeatability. Other equipment may be used, but should be evaluated to determine the impact on test measurement uncertainty. All equipment should be calibrated regularly and calibration records maintained. The types of tools required are primary bullets. Sub-bullets provide a list of options meeting the primary bullet requirements. Specifications provided are based on a 2 in. diameter circular contamination area.

- **Contaminant Delivery Tool:** the tool used to apply a specified amount of agent to the coupon surface. The tool must be capable of delivering the specified contaminant volume to the coupon surface. Tools with repeater capabilities are recommended to ensure identical replicate samples. The typical delivery volumes for a 2 in. diameter circular contamination area range from 1 to 20 microliters (μL) which is equivalent to a 1 and 10 g/m^2 starting challenge, respectively. Example: the core coupon test specifies using a total contamination volume of 2 μL delivered as two 1 μL drops for a 1 g/m^2 starting challenge.
  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred to prevent cross-

contamination if the tool is used for multiple procedure steps, dosing solutions or contaminants. Positive displacement pipettes are also recommended for highly viscous materials as the positive wiping action of the piston against the capillary wall assures accurate dispensing and avoids any carry-over. Also best suited for pipetting volatile liquids. Smallest delivery volume, based on survey of commercial items with repeater capability, is about 1 µL. Pipettes used for the purpose of contaminant delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.

  - Syringe: Positive displacement tool best suited for the delivery of smaller drop volumes. Smallest delivery volume based on survey of commercial items with repeater capability is about 0.2 µL. Syringes to be used for the purpose of contaminate delivery should have a maximum inaccuracy of 1% and a maximum imprecision of 1% of the volume being measured.

  - Computerized Dispensing System: Automated tool with ability to deliver specific drop volumes and surface coverage patterns. Based on a review of commercial items, the smallest delivery volume is approximately 0.35 nL with repeatability < 1%. The manufacturer performance specifications should be reported and evaluated against acceptable measurement uncertainty for the particular test.

- **Extraction Solvent Delivery Tool:** Tool for the delivery of specific volumes of solvent to the extraction container. A repeater tool is recommended for the coupon studies since multiple coupon replicates are used in each test. The typical delivery volume for extraction of 2 in. diameter circular disk is 20 mL.

  - Bottle-Top Dispenser: These are precision liquid dispensers that can be connected to solvent and rinse water bottles. These tools are available in different configurations based on liquid to be dispensed. The appropriate tool should be used to dispense organic solvents. Common brands include Dispensette and Brinkman. Bottle top dispensers to be used for the purpose of solvent delivery should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 5 and/or ASTM E 1154 for the volume being measured.

- **Sample Dilution and Analytical Standard Preparation Tools:** the tool used to prepare sample dilutions. The tool must be capable of delivering the specified liquid volume. Single dispensing (i.e., not repeater) tools are preferred as these typically have higher accuracy and precision. Fresh tips must be used for each sample to prevent cross-contamination.

  - Pipette: The tool with the largest range of delivery volumes. Positive displacement pipettes with disposable tips preferred for work with chemical contaminants to prevent cross-contamination. Pipettes used for the purpose of sample dilution or analytical standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured.

  - Volumetric Glassware: volumetric flasks should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69.

- **Analytical Chromatography Equipment:** The samples generated in this test method are analyzed under test Procedure 7-F. The test facility must have the capability to quantitatively analyze the samples immediately after testing. Gas and liquid

chromatography equipment fitted with mass-selective detectors are preferred. Other quantitative detectors may be used.

MATERIALS AND SMALL EQUIPMENT

- **Aluminum foil:** Aluminum foil is typically used to line work space, protect kilogram masses from being contaminated, etc.
- **Analytical vials and caps**: Appropriate analytical vials for use on the chromatographic equipment. The vial cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.
- **Coupon(s):** Test sample representative material surface.
- **Coupon tray:** Optional item for the handling and movement of coupons during testing.
- **Decontaminant bath**: Used to collect spent disposable test items (e.g., pipette tips, coupons, analytical vials and caps, etc.) in a solution that will neutralize any agent left on the material. For most chemical agents, this bath contains excess volume of household bleach to submerge items.
- **Extraction containers**: The procedure involves the extraction of the coupon. A glass container such as a vial or jar of sufficient size to hold both the coupon and extraction solvent volume is required. The container cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample. Use of plastic containers is not recommended for chemical agent testing.
- **General laboratory items:** Items may include glassware (vials, flasks, cylinders, bottles, beakers, jars, etc.), paper towels, beakers, vials, spatulas, parafilm, etc
- **Petri dishes:** are typically used during the aging step to cover the coupon surface to minimize evaporative loss. Can also be used as sample holder.
- **Sample handling tools:** tools for the handling of coupons during testing which may include forceps, tweezers or tongs.
- **Standard laboratory record keeping items:** Record keeping items may include computer, data test form, laboratory notebooks and writing utensils.
- **Timing device(s):** Test method requires accurately timing key steps. Digital timers reporting in minutes and seconds are preferred.
- **Transfer pipette**
- **Optional items:** Items that may be used include analytical balance.

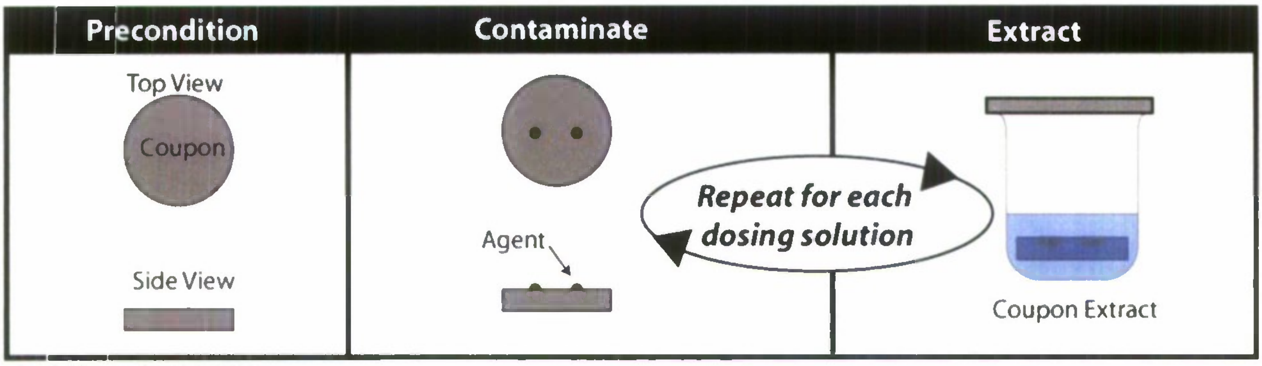
SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

The procedure specifies the sample handling, measurement and reporting tasks. Additional steps for moving samples between work spaces (i.e., sample containment and transfer between

engineering controls / hoods), sample decontamination and waste disposal steps are not presented here. Those steps should be added, as appropriate, based on the method user's facility safety and regulatory requirements. The extraction efficiency function determined by this method is valid for the tested material lot and extraction method used. Lot-to-lot variations in test materials may exist and should be verified.



sketch Mantooth-Lalain 2007

Figure 7D-1. Coupon Extraction Efficiency Test Sketch.

1.0 Test Preparation Tasks

The method user should ensure that all necessary equipment, materials, reagents and analytical capabilities are available for the test. All equipment should be confirmed operational prior to start of test. Preparation tasks for this method may include:

- Turning on equipment that will need to thermally equilibrate (i.e., environmental boxes).
- Completion of test area setup, labeling (i.e., vials, trays, jars) and other associated pretasks that can be performed prior to the start of testing.
- Coupon inspection: all coupons should be cleaned (if required) and inspected to remove any unacceptable specimens prior to the start of testing.
- Check that all calibrated equipment is current (e.g., has not passed expiration date).
- Recommended that contaminate equilibrate to room temperature prior to use.

This procedure can be applied to multiple coupons during a single test session. In that case it is important that each coupon is treated identically. The use of timing charts staggering contamination, decontamination and rinse test times is strongly encouraged as subtle differences in coupon treatment can contribute to data scatter.

The recommended number of replicates is a minimum of five coupons per test condition and five dose-confirmation samples per contamination set.

The test is performed at the conditions at which the extraction will occur.

2.0 Prepare Dosing Solutions

2.1 Up to seven dosing solutions are prepared to provide various delivered mass values. Identify the smallest mass on the surface of the test material (e.g., coupon, dental dam) for the following two situations.

2.1.1 Multiply the smallest requirement surface concentration by the surface area of the test material to calculate the mass on coupon (e.g., JPID 2003

objective for VX is 0.005 mg/m^2 x 0.00202 m^2 x 10^6 ng/mg = 10.1 ng on coupon). Divide the mass on coupon by 10.

$$Mass_{\text{Requirement}} = \frac{\text{Requirement} \cdot \text{Surface Area}}{10} \cdot 10^6$$

2.1.2 The second situation to consider is the detection limit of the analytical method. Multiply the LOQ (ng/mL) of the most sensitive analytical method used (e.g., the LOQ of 0.05 ng/mL for VX on LC-MS/MS) by the extraction volume (mL) as defined by

$$Mass_{\text{Analytical}} = LOQ \cdot Volume_{Extract}$$

2.1.3 The value $Mass_{Min}$ is defined as the smaller of $Mass_{Requirement}$ or $Mass_{Analytical}$.

Note: If $Mass_{Requirement}$ is less than $Mass_{Analytical}$, this implies that the analytical quantitation limit cannot detect an order of magnitude below the requirement.

2.2 Determine the mass of contaminant to deliver to the coupon

2.2.1 The selection of masses to be delivered is based on the fitting of the empirical EE models. The following guidance will deliver a model that should represent the system.

2.2.2 Calculate the mass to be delivered using the following table as guidance

2.2.3 Calculate the concentration of the solution to deliver the same contamination profile as used in testing (e.g., Procedures 7-A and/or 7-C) to contaminate the coupon. For example, if two 1.0 µL drops are used to contaminate the coupon with neat agent for testing, use two 1.0 µL drops for this test. Solution concentration (ng/mL) can be calculated from the $Mass_{Delivered}$ (ng), number of drops (n), and drop volume (V in µL) as

$$\text{Sln. Conc} = \frac{Mass_{Delivered}}{nV \cdot 10^{-3}}$$

Guidance Formula	Example: VX $Mass_{Delivered}$ $Mass_{Min}$ = 1.00 ng	Resulting Nominal Solution Conc. (ng/ml) For 2 x 1.0 µL drops
$Mass_{Min}$ × 2	2	1,000
$Mass_{Min}$ × 5	5	2,500
$Mass_{Min}$ × 10	10	5,000
$Mass_{Min}$ × 33	33	16,500
$Mass_{Min}$ × 100	100	50,000
$Mass_{Min}$ × 1,000	1,000	500,000
$Mass_{Min}$ × 10,000	10,000	5,000,000

2.3 Prepare the dosing solutions

2.3.1 The solutions can be prepared either volumetrically or gravimetrically. The discussion here is for volumetric addition. This procedure could be scaled up to use volumetric glassware. The approach here was to reduce total agent consumption and waste generated. An example solution preparation table for VX using an 89.5% pure neat agent is shown. Higher concentration solutions are prepared from neat agent, and then serially diluted to create lower concentration solutions.

Note: Extraction efficiency is determined from mass delivered which is measured by dose-confirmation samples (i.e., not solution concentration x dose volume); this approach minimizes any bias introduced by the dosing tool or solution preparation technique and reduces the accuracy required to prepare the dosing solutions.

2.3.2 The solutions are prepared by the placement of a set volume of solution dispensed via pipette into a vial to which the appropriate volume of solvent is added via pipette.

2.3.3 The vial is immediately capped using a PTFE/Teflon lined cap.

2.3.4 The vial is inverted three times for thorough mixing.

Agent	**VX**
Density (ng/ml)	1,008,300,000
Mole % Purity	89.5%
Corrected Density	902,428,500

Standard Name	Nominal Conc (ng/mL)	Stock Solution	Volume Stock Sln (mL)	Solvent Volume (mL)	Total Vol (mL)	Corrected Conc (ng/mL)
SolutionA	50000000	Neat	0.059	1.000	1.059	50,276,942
SolutionB	5000000	SolutionA	0.112	1.000	1.112	5,063,865
SolutionC	500000	SolutionB	0.110	1.000	1.110	501,824
SolutionD	50000	SolutionC	0.111	1.000	1.111	50,137
SolutionE	16500	SolutionC	0.034	1.000	1.034	16,501
SolutionF	5000	SolutionD	0.112	1.000	1.112	5,050
SolutionG	2500	SolutionD	0.053	1.000	1.053	2,524
SolutionH	1000	SolutionE	0.065	1.000	1.065	1,007

2.4 Complete the required reporting for this section

3.0 Contaminate Coupons

3.1 The contamination approach should match that used in the core test Method 7-A. Identify contamination density to include number of drops, drop volume and deposition pattern. Test Procedure 7-A Option C cannot be performed for this test as the amount delivered cannot be tightly measured.

OPTION A (core test): contamination density is 1-1.2 g/m^2 applied using pipette, syringe or equivalent tool as 1 µL drops placed in the 2 in. circular test area non-touching. For traditional agents, this is typically two drops resulting in a 1 g/m^2 contamination density for VX and GD, and a 1.2 g/m^2 contamination density for HD if agents are of CASARM or high purity grade.

OPTION B (core test, variable condition): variable contamination density is typically between 1 to 10 g/m^2 applied using pipette, syringe or equivalent tool as variable sized

drops within the 2 in. circular test area. The drops might touch depending on the desired deposition pattern.

3.2 Set tool to appropriate drop volume

- Note: the pipette volume should not be changed within a set of procedures. Tests have shown that changing tool dispensing volumes can affect delivery. If changes must be made, dose-confirmation samples must be prepared after each change.

3.3 Fit pipettor with clean appropriate pipette tip

3.4 Load contaminant delivery tool with dosing solution in accordance with manufacture's directions.

3.4.1 Deliver to the surface the appropriate number of drops to achieve the contamination density.

- Note: If the repeater pipette is at rest for more than a few seconds, the pipette should be cleared by dispensing a drop onto a reject coupon, adsorbent paper (M8 paper for surety tests) or equivalent. Solvent and agent evaporation can occur in the tip affecting the next dose from the tool.

3.4.2 Allow the solvent to evaporate which is typically 5 to 20 seconds, do not exceed 60 seconds.

3.4.3 Add 20 mL of extraction solvent

3.4.4 Cap jar with PTFE/ Teflon-lined lid.

3.4.5 Gently swirl container to mix contents.

3.4.6 Coupon will remain in extraction solvent for 60 min. Note: other extraction times can be used; the extraction time used here should agree with extraction time used for testing (e.g., Procedures 7-A and/or 7-C).

3.4.7 Gently swirl container to mix contents.

3.4.8 Using a clean, disposable pipette load the analytical vial with aliquot of extractant solution.

3.4.9 Repeat steps 3.4.1 through 3.4.8 as needed for total number of coupons.

3.4.10 Prepare the "dose confirmation" sample. At least five replicated samples are recommended.

3.4.10.1 Deliver to a scintillation vial the sample number of agent drops.

3.4.10.2 Add 20 mL of extraction solvent.

3.4.10.3 Cap vial

3.4.10.4 Thoroughly mix contents by inverting vial three times.

3.4.10.5 Using a clean, disposable pipette load the analytical vial with aliquot of extractant solution.

3.5 Using a clean, pipette tip, repeat steps 3.3 and 3.4 for each solution.

3.6 Complete the required reporting for this section.

4.0 Chromatographic Analysis for remaining agent

4.1 Samples are analyzed based on guidance in Procedure 7-F.

- Dose confirmation
- Coupon extract

4.2 Sample dilution may be required for sample to be within the analytical method calibration range. This is typically true for the dose-confirmation samples.

4.3 Obtain list of analytical results in ng/mL which already accounts any additional dilutions beyond initial extraction.

4.4 Complete the required reporting for this section.

5.0 Perform Calculations

5.1 Obtain the analytical results for

- Dose confirmation
- Coupon extract

5.2 Perform calculations.

5.3 Complete the required reporting for this section.

CALCULATIONS

1.0 Prepare Results Table

1.1 Obtain the chromatography data in ng/mL for the coupon extract (**CE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis. Due to the dynamic range of the data included in this analysis several analytical methods may be used to analyze the samples. If there is a sample that reports a non-detection value and there is an analytical method with a lower detection limit, the sample should be re-run on the more sensitive method.

1.2 Calculate 'Analyte Mass Recovered' ***Rec***.

For each coupon extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\textbf{\textit{Rec}} \text{ (in ng)} = \mathbf{CE_E \times EV} \qquad (1)$$

- **Note**: Any data that is below the analytical method lower quantitation limit should not be reported or used in the fitting and analysis.

1.3 Calculate 'Analyte Mass Delivered' ***Del***.

For each dose confirmation sample extract convert the analytical results in ng/mL to mass results in ng by multiplying the extraction solvent volume (**EV**) in mL. For the method as written, the extraction solvent volume is 20 mL.

$$\textbf{\textit{Del}} \text{ (in ng)} = \mathbf{DC_E \times EV} \qquad (2)$$

1.4 Calculate the average and standard deviation of the delivered mass for all replicates of each solution. (Acceptance criteria: the relative standard deviation (std/avg) must be < 15%)

1.5 Prepare results table for each dosing concentration listing the target mass on coupon, delivered and recovered results.

1.6 Calculate the Extraction Efficiency (**EE**) for each sample which is calculated per Equation 3.

$$\mathbf{EE} = \boldsymbol{Rec} / \boldsymbol{Del} \qquad (3)$$

1.7 Two calibration models will be calculated, the following procedures will identify which calibration curve best represents the extraction performance.

2.0 Prepare the Independent and Relative Recovery (IRR) EE Calibration Curve

2.1 Calculate 1 / **Del** from the average calculated in step 1.4.

2.2 For each replicate sample plot 1 / **Del** vs. **EE** (calculated in step 1.6).

- **Note**: do not calculate an average EE for each dose solution, the empirical fitting uses each **Rec** data point.

2.3 Apply a linear regression to the data.

2.4 The IRR EE calibration curve assumes the following relationship where R is a relative recovery term and I is an independent loss term. The slope obtained from step 2.3 equals -I, R equals the intercept from step 2.3

$$\boldsymbol{Rec} = (\boldsymbol{Del} \times \boldsymbol{R}) - \boldsymbol{I} \qquad (4)$$

I = -slope (of 1/Del vs. EE)

R = intercept (of 1/Del vs. EE)

2.5 Calculate the EE as a function of delivered mass for the calibration curve:

$$\boldsymbol{EE_{IRR}(Del)} = \mathbf{R} - \mathbf{I} / \mathbf{Del} \qquad (5)$$

2.6 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = (\mathbf{EE} - \mathbf{EE_{IRR}(Del)})^2 \qquad (6)$$

2.7 Calculate the sum of the square of the errors, this term is used later to select which calibration curve to use.

$$\mathbf{SSE_{IRR}} = \Sigma\sigma^2 \qquad (7)$$

2.8 If this EE calibration curve is chosen, the EE corrected mass is calculated by

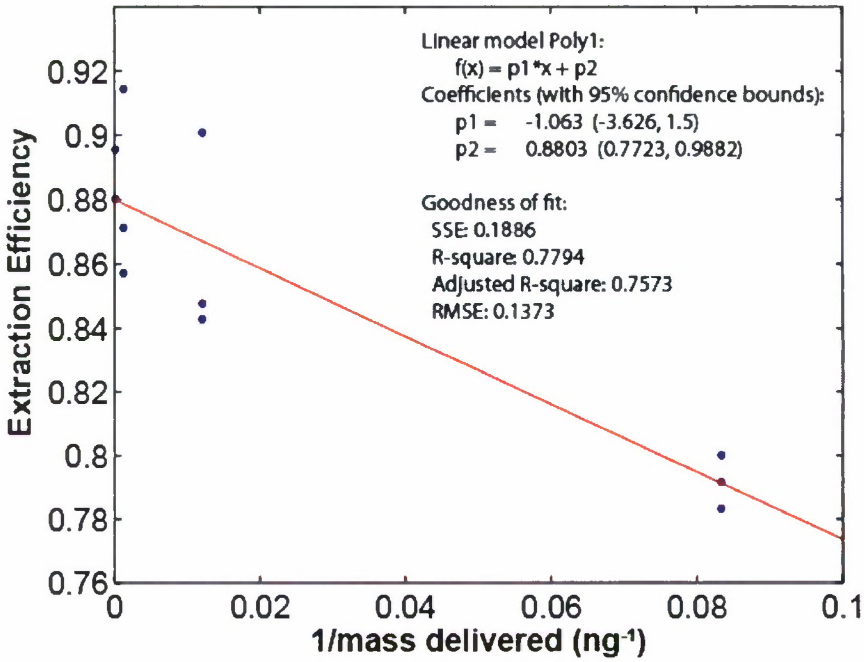
$$\mathbf{Mass_C = (Mass_M + I) / R} \qquad (8)$$

Note: if the extracted mass (M_E) is below the limit of quantitation (LOQ), the corrected mass should be reported as below quantitation or below detection.

Sample Calculation of Step 2.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	1 / Mass Delivered (ng^{-1})	Mass Recovered (ng)	Extraction Efficiency
15	12.0 ± 1.4 [11.6%]	0.083031	9.6	0.795
			9.4	0.778
			9.5	0.785
100	82.7 ± 2.8 [3.4%]	0.012099	70.1	0.848
			69.7	0.843
			74.5	0.901
1,000	834.3 ± 16.6 [2.0%]	0.001199	726.9	0.871
			715.0	0.857
			762.7	0.914
10,000	8538.8 ± 313.3 [3.7%]	0.000117	7,646.5	0.896
			15,431.8*	1.807*
			7,515.3	0.880

*identified as statistical outlier



Calibration Curve Coefficients:

I = -slope = -p1 = 1.063 (ng)

R = intercept = p2 = 0.8803 (unitless)

3.0 Prepare the Power Law (PL) EE Calibration Curve

3.1 Calculate log (**Del**) from the average calculated in step 1.4.

3.2 Calculate log (**Rec**) for each replicate sample calculated in step 1.2.

3.3 For each replicate sample plot log (**Del**) vs. log (**Rec**). Note: do not calculate an average log (**Rec**) for each dose solution, the empirical fitting uses each individual data point.

3.4 Apply a linear regression to the data.

3.5 The PL calibration curve assumes the following relationship where the slope (m) and intercept (b)

$$\boldsymbol{Rec = 10^{b} \times Del^{m}} \qquad (9)$$

3.6 Calculate the EE as a function of delivered mass for the calibration curve:

$$\boldsymbol{EE_{PL}(Del) = (10^{b} \times Del^{m}) / Del} \qquad (10)$$

3.7 Calculate the square of the residual (error) for each replicate EE data point (Calculated in step 1.6) with respect to the EE calibration curve:

$$\sigma^2 = \boldsymbol{(EE - EE_{PL}(Del))^2} \qquad (11)$$

3.8 Calculate the sum of the square of the errors

$$\boldsymbol{SSE_{PL} = \Sigma\sigma^2} \qquad (12)$$

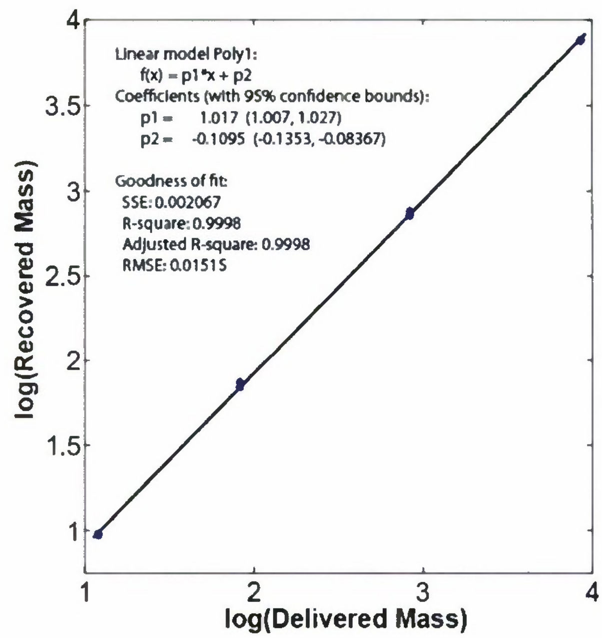
3.9 If this EE calibration curve is chosen, the EE corrected mass is calculated by

$$\boldsymbol{Mass_C = (Mass_M / 10^{b})^{1/m}} \qquad (13)$$

Sample Calculations of Step 3.0

Target Mass (ng)	Mass Delivered (ng) [RSD]	Log(Del)	Mass Recovered (ng)	Log(Rec)
15	12.0 ± 1.4 [11.6%]	1.079	9.6	0.9809
			9.4	0.9718
			9.5	0.9754
100	82.7 ± 2.8 [3.4%]	1.918	70.1	1.845
			69.7	1.843
			74.5	1.871
1,000	834.3 ± 16.6 [2.0%]	2.921	726.9	2.861
			715.0	2.854
			762.7	2.882
10,000	8538.8 ± 313.3 [3.7%]	3.931	7,646.5	3.883
			15,431.8*	4.188*
			7,515.3	3.875

*identified as statistical outlier



Calibration Curve Coefficients:

m = slope = p1 = 1.017 (unitless)

b = intercept = p2 = -0.1095 (unitless)

4.0 Select the EE Calibration Curve

4.1 Compare the SSE values for each calibration curve. The calibration curve with the smaller SSE provides the better fit.

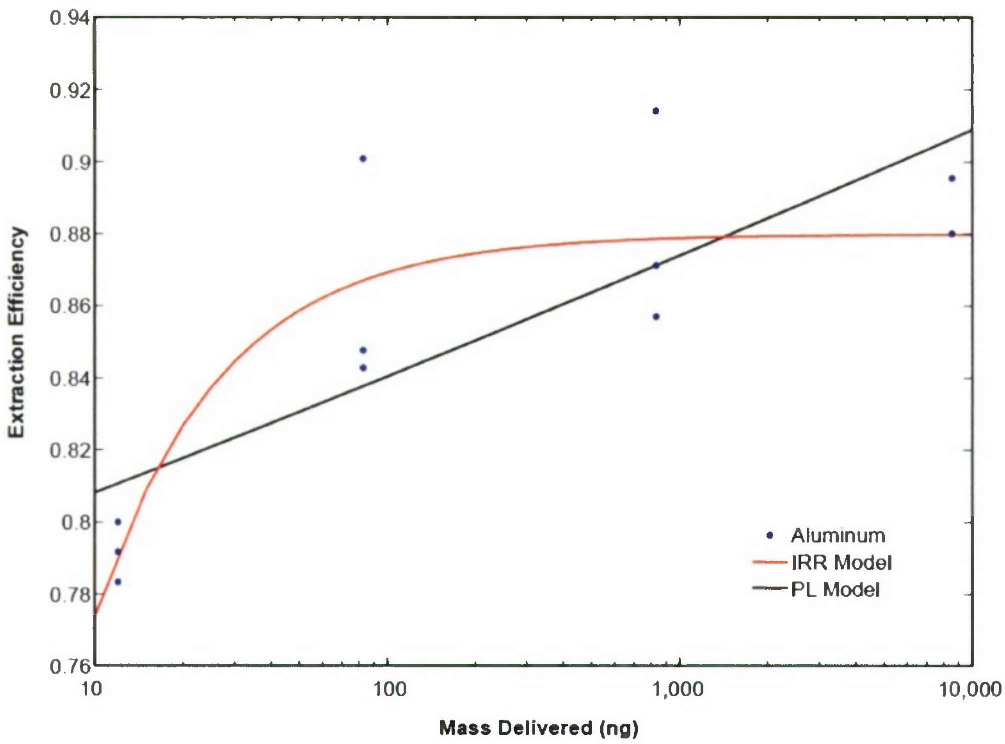
4.2 Plot **Del** vs. **EE**, and **Del** vs. **EE$_{Model}$** (**Del**) to visually confirm the model fits the data.

4.3 For any calculations that use extraction efficiency correction use Equation 8 if the IRR calibration curve was selected or Equation 13 if the PL calibration curve was selected.

- **Note**: the EE calibration curve has similar 'rules' of implementation as an analytical instrument calibration curve; recovered masses applied to the EE calibration curve that are significantly outside of the tested mass values may not return accurate results.
- **Note:** Extrapolation of the EE calibration curve above the tested range must be handled with caution. Multiple EE calibration curves may be needed to test from contamination density (e.g., 1- to 10 g/m^2) extractions down to requirements (e.g., 0.05 mg/m^2) level extractions. This is especially true for reduction in starting challenge calculations where extracted masses may be large.
- **Note**: Due to the limitations of EE testing caused by evaporation and other loss mechanisms, extrapolation to ranges below the test range qualifier will be allowed at this time.

4.4 Report which EE calibration curve was used and the coefficients used in the calibration.

Mass Del (ng)	**Data EE**	**IRR Model EE**	**IRR Residual (σ)**	**IRR σ^2**	**PL Model EE**	**PL Residual (σ)**	**PL $(\sigma)^2$**
12.0	0.7947	0.7917	0.0029	8.614E-6	0.8107	-0.0160	2.567E-4
	0.7781		-0.0136	1.842E-4		-0.0325	1.058E-3
	0.7847		-0.0070	4.857E-5		-0.0259	6.722E-4
82.7	0.8480	0.8675	-0.0195	3.789E-4	0.8377	0.0103	1.054E-4
	0.8432		-0.0243	5.893E-4		0.0055	2.974E-5
	0.9009		0.0335	1.119E-3		0.0632	3.992E-3
834.3	0.8713	0.8790	-0.0077	5.933E-5	0.8713	0.0000	1.474E-9
	0.8570		-0.0220	4.840E-4		-0.0143	2.033E-4
	0.9142		0.0352	1.238E-3		0.0429	1.843E-3
8538.8	0.8955	0.8802	0.0153	2.350E-4	0.9064	-0.0109	1.193E-4
	1.807*		N/A	N/A		N/A	N/A
	0.8801		0.0000	1.295E-9		-0.0263	6.911E-4
Goodness of Fit			**SSE**	**0.00435**		**SSE**	**0.00897**
			RMSE	**0.01988**		**RMSE**	**0.02856**
			R^2	**0.8151**		**R^2**	**0.6057**
			Corr. Coef.	**0.9028**		**Corr. Coef.**	**0.7783**



TEST REPORTING

The following information must be documented in the test report for this procedure. The test reporting section is shown as three parts: experimental, test-specific, and reporting statement. The experimental reporting requirements capture the tools and materials used in the test. In many cases, the experimental section will be the same from test to test within a program. For this reason, this information is best documented as a formal experimental section of the test report. Any variations for a specific test should be clearly documented. The test specific report requirements capture what occurred during the test. This information should be reported for each test. This information is typically best captured with the test results in the test report. The reporting statement is suggested language for expressing the test result with the key test information for proper context.

EXPERIMENTAL SECTION: The test report must contain an experimental section documenting the specific equipment used to execute this procedure. The experimental section includes the reagents, equipment, materials, and a detailed test summary.

REAGENTS

- **Contaminant Information:** provide for each contaminant used the contaminant name, source, purity and lot.
- **Extraction solvents:** provide for each extraction solvent used the source, grade, purity and lot.

EQUIPMENT

- **Contaminant Delivery Tool**

- Tool identification including manufacturer, model number, and volume dispensing range.
  - Tool performance specifications including accuracy and any other conformance specifications (e.g., ISO 8655 or ASTM E1154).
  - Calibration status, which may include a general description of the laboratory process for ensuring the tools used are calibrated or the date the next calibration is due.
  - For developmental items or tools without performance specification standard the following information must be provided: tool description, source, laboratory determined accuracy and precision, and a description of how tool reproducibility from test-to-test is ensured.
- **Extraction Solvent Delivery Tool:** *see contaminant delivery tool listing.*
- **Sample Dilution and Analytical Standard Preparation Tools:** *see contaminant delivery tool listing.*
- **Analytical Chromatography:** provide a description of the entire unit configuration including for major components the component description (e.g., detector, injection system, etc.), manufacturer, and model number.

MATERIALS

- **Coupons:** For each material used provide stock material description including description, source, part number, description of the preparation method, coupon acceptance inspection method, and lot number for prepared coupons. Also include the age since preparation for painted surface since some coatings can take up to one year to fully cure.

DETAILED TEST SUMMARY: Description of overall process performed, including test location, any sample transporting, or explanation of how the process ensured coupons were treated identically for multiple coupon tests, and total number of replicate samples tested. The treatment and test timeline noting specific time intervals for each task must be provided. Any deviations from the published procedure must be documented.

TEST SPECIFIC: The test report must report the following information. For test programs where many parameters (e.g., option selection, drying process, etc.) may be identical test-to-test, the repetitive information can be documented as part of the experimental section to conserve space. However, the specific test measurements must be documented with the test results.

- **Contamination**
  - Option used (A, B or C)
    - For Option C: a description of how the contamination was performed.
  - Contamination density in g/m^2.
  - Total agent volume in microliters (μL) per coupon.
  - Agent drop volume size(s) in microliters (μL) per coupon.
  - Description of drop deposition pattern for contamination using more than one applied drop. A drawing or photograph is recommended.
  - Test location temperature and relative humidity during contamination.
  - Contaminant temperature at time of contamination.
  - Description of contaminant handling. For example, if the contaminant is applied "cold" or "warm" provide a description of how contaminant was chilled or warmed. If contaminant was warmed to room temperature and applied, note as such.
- **Dose Solution Preparation**: include the number of dosing points, list of target delivered mass per test surface (e.g., coupon, contact sampler) in nanograms, corresponding list of nominal solution concentrations in nanograms per milliliter (g/mL), and a description of dosing solutions preparation.

- **Residual Agent Measurement:** include the extraction solvent and extraction time.
- **Chromatographic Analysis:** Include a description of the analytical method used, use and acceptance for CCV samples, calibrated range, method LOD and LOQ, calibration curve fitting and goodness of fit parameters as expressed in Method 6-H. Provide the analytical results for the coupon test results in nanograms per coupon and "dose confirmation" sample mass in nanograms.
- **Calculation Reporting Criteria**
    - Summary data table containing the following information.
        - Data in ng/mL for the coupon extract (**CE_E**) and the dose-confirmation samples (**DC_E**) that has been corrected for any dilutions performed between sample collection and analysis.
        - Analyte mass recovered (***Rec***) results in ng for each test replicate for each dosing solution.
        - Delivered mass results (***Del***) in ng for each dosing solutions, average Del and RSD.
        - Extraction efficiency (**EE**) calculated for each sample.
        - Which EE calibration curve was selected - Independent and Relative Recovery (IRR) or Power Law (PL).
        - The calibration curve slope and intercept.
        - Provide the selected calibration curve.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

The decontamination panel test is a measurement dealing with multiple forms of mass transport involving competing processes that move the agent to various compartments of the system including evaporation (into the air), sorption (into the material), chemical reaction (anywhere in system) and physical removal (from the material). Conducting representative tests to enable the comparison of results requires careful control and measurement of test parameters. For example, minor differences in contaminated surface coverage can have a large impact on test results. For this reason the following guidance is provided to asses the acceptance criteria for a test and discusses the impact each variable has on the system. These factors are especially important for cases were decontamination test results are compared to baseline test results or other decontaminant tests.

The end use of the data may determine many of the test parameters and should be established between the testing facility and the test sponsor. For any given test, the environmental parameters (temperature, and relative humidity), event timing (duration of contaminated coupon aging, decontaminant residence time, coupon preconditioning, etc.), contaminant, decontaminant, skin simulant, etc. are determined and directed by the test sponsor. If any condition specified by the test sponsor or data acceptance criteria cannot be met, the test sponsor shall be contacted immediately. If the test sponsor accepts the test results under the conditions the test was run, then the acceptance should be documented. If the test results are not accepted by the test sponsor, then the test must be rerun.

During data analysis, the data may be tested for outliers. A standardized method, such as ASTM E 178, should be used. Although ASTM E 178 discusses multiple methods to test for outliers, the method discussed in sections 6.1 though 6.2 is recommended. Data points determined to be an outlier may be excluded from statistical data analysis and should be flagged as being excluded, but must be reported along with the appropriate data set.

There are documented industrial cases where a test method has a verified test error of < 10%; however testing of specific materials generates reported test errors of > 100%. This in not always an indication of a poorly executed test, but that the material under test may be highly variable. It is recommended that large test result variances observed in decontaminant testing are evaluated for material variability rather than assuming faulty test methodology. Material variability could give false sense that retesting is needed, when the effect is real and should be reported.

Recommended Data Acceptance Parameters and Rationale

Delivered Mass: The delivered mass for the determination of the extraction efficiency test should produce analytical results with a RPD < 15%.

- Rationale: Due to the number of tools used and steps involved in preparing the dosing solutions, the most accurate method to calculate the delivered mass is to directly measure exactly what was delivered to the sample. This enables an accurate method to determine the extraction efficiency per test sample.

EE Model: The EE calibration model selected should provide a best fit to the data. Though some materials may provide a significant distribution of results, it is recommended that an average RPD value for a model is <15%. However, it is recognized that some materials may never meet this criteria. In all cases the average RPD value should be reported.

- Note: the EE calibration model assumes all loss is due to incomplete extraction. No correction is included that accounts for 'depth' in the material that may be harder to extract.

REVISION HISTORY

March 2008: original method.

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Test Procedure 7-E: Data Calculation Method to Report Vapor Hazard

SUMMARY OF PROCEDURE

The objective of decontaminant performance evaluations is to use the test data to make conclusions regarding the decontaminant performance. These results may be compared to requirement documents or by compared to current/other decontaminants. This section provides the detailed calculations to determine the vapor concentration as a function of time, the vapor emission factor, the vapor emission factor model (best metric to compare vapor data to between decontaminants), scenario vapor concentration, and the vapor toxic load to determine hazard to unprotected personnel.

The vapor test in Section 7-A generates several vapor samples (i.e., tubes) that are collected over a specified time period. The vapor concentration as a function of time is calculated for each sample. This measured vapor concentration is ***not*** appropriate to compare to requirements documents and does ***not*** correspond to the vapor concentration to which unprotected personnel would be exposed.

The emission factor of the coupon is calculated from the vapor concentration data. Using a fitting technique, the emission factor model is determined. The emission factor model is used to scale the vapor data to a scenario. The scenario-based vapor concentration is appropriate to compare to requirements documents and is used to calculate a vapor hazard using a toxic load model (i.e., the ten Berge equation).

TERMINOLOGY

Terminology, listed alphabetically, specific to this test procedure are provided in the bulleted list.

- **analytical sample -** liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **air flow rate, chamber** – The air flow rate through the vapor chamber during the experiment, reported in mL/min.
- **air flow rate, sampling** – The air flow rate through the solid sorbent tube during sample collection, reported in mL/min, may be different than chamber air flow rate depending on chamber configuration.
- **chemical agent** - is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **chamber vapor concentration** – the vapor concentration measured from the vapor chamber. This concentration does not correspond to the vapor concentration to which unprotected personnel would be exposed and should not be compared to requirements documents.
- **confidence interval** – is a calculated range for a data set that future results are likely to fall between.
- **contamination set -** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.

- **coupon** - test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area** – the geometric area of the surface of a coupon (for a 2 in diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **hazard** - A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **panel** – *see coupon.*
- **relative standard deviation (RSD)** – the standard deviation of a data set divided by the mean of the data set.
- **requirement levels** - the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **scenario vapor concentration** – the vapor concentration calculated based on a scenario using the emission models for all materials involved in the scenario. This vapor concentration does correspond to the vapor concentration to which unprotected personnel would be exposed and can be compared to requirements documents.
- **surface coverage** – usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **time, tube pulling** – the length of time that air was flowing through a solid sorbent tube.
- **time, midpoint** – the time representing when a sample was collected as calculated by tube initial time + ½ tube pull time.
- **time, initial** – the time representing the start of air flow (sample collection) for a tube.
- **test condition** - for a specific agent – material- decontaminant set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.

REFERENCED DOCUMENTS

- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document." and references therein.

VAPOR DATA CALCULATION METHOD

1.0 Calculate the Chamber Vapor Concentration

The Chamber Vapor Concentration (mg/m^3) is calculated from the contaminant mass on the solid sorbent tube (determined by a validated analytical technique such as TD-GC-MSD), the sampling air flow rate through the tube (note, if a split it used to sample the chamber use the sample air flow rate, *F*, not the chamber air flow rate, *Q*), and the sampling time. All three values must be accurately measured to ensure accurate calculation of the chamber vapor concentration. This concentration corresponds to the concentration of vapor in the chamber at the midpoint sampling time (t_m), defined later. This chamber concentration should not be

compared to a requirement and does not correspond to the vapor concentration to which unexposed personnel may be exposed. The chamber vapor concentration is determined using Equation 1.

Equation 1

$$C = \frac{m/100{,}000}{V} = \frac{m}{t_t F/1{,}000{,}000}$$

where

C	= vapor concentration (mg/m^3),
m	= analyte mass on tube (ng),
V	= sampled air volume (m^3),
t_t	= total tube sampling time (min.),
F	= sampling air flow (mL/min.).

Calculate the chamber vapor concentration, C (mg/m^3) for each tube. An example data table is shown as Table 7E-1.

Table 7E-1. Vapor test case study analytical results.

Vapor Chamber (number)	Tube (number)	Mass on Tube (ng)	Tube Pull Time (min.)	Air Flow Rate (mL/min.)	Air Volume (m^3)	Vapor Concentration (mg/m^3)
1	0	10	60	300	0.0180	0.001
1	1	1115	5	300	0.0015	0.743
1	2	NQ	5	300	0.0015	NQ
1	3	825	10	300	0.0030	0.275
1	4	805	15	300	0.0048	0.179
1	5	851	25	300	0.0075	0.0113
1	6	1314	60	300	0.0180	0.073
2	0	9	60	300	0.0180	0.000
2	1	976	5	300	0.0015	0.650
2	2	NQ	5	300	0.0015	NQ
2	3	769	10	300	0.0030	0.256
2	4	735	15	300	0.0048	0.163
2	5	745	25	300	0.0075	0.099
2	6	1098	60	300	0.0180	0.061
3	0	33	60	300	0.0180	0.002
3	1	1048	5	300	0.0015	0.0699
3	2	NQ	5	300	0.0015	NQ
3	3	751	10	300	0.0030	0.250
3	4	717	15	300	0.0048	0.159
3	5	708	25	300	0.0075	0.094
3	6	1027	60	300	0.0180	0.057

2.0 Generate Tube Pull Timing Information Table

The sorbent tube pull time is described as four terms that are used for different portions of the calculation. The four terms total (t_t), initial (t_i), final (t_f) and midpoint (t_m) are illustrated in Figure 7E-1. The values in this table should be the actual experimental times.

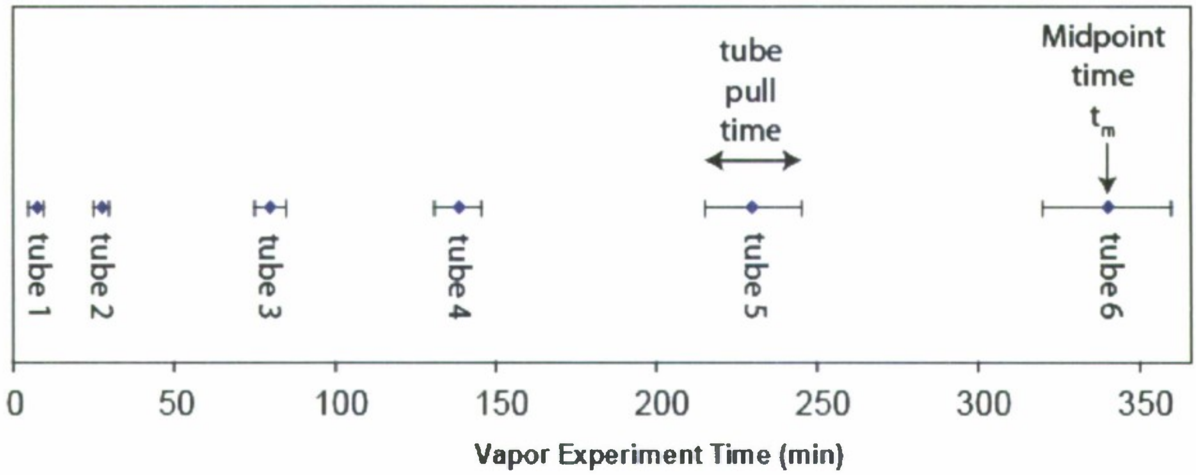

Figure 7E-1. Sample pull schedule.

The time of the vapor concentration measurement will be calculated as the midpoint tube pull time. An example timing event table is provided as Table 7E-2.

Table 7E-2. Vapor case study timing events

Vapor Chamber (number)	Tube (number)	t_i, Initial Tube Pull Time (min.)	t_f, Final Tube Pull Time (min.)	t_t, Total Tube Pull Time (min.)	t_m, Midpoint Tube Pull Time (min.)
1	0	-90	-30	60	-60.0
1	1	5	10	5	7.5
1	2	25	30	5	27.5
1	3	70	80	10	75.0
1	4	130	145	15	137.5
1	5	215	240	25	227.5
1	6	300	360	60	330.0

3.0 Calculate the Emission Factor

The emission factor (mg m^{-2} min^{-1}) is calculated from the chamber vapor concentration as a function of time and other experimental parameters. The ideal way to calculate an emission factor, E(t), is to directly fit an emission model in the mass balance differential equation as given by Equation 2.

Equation 2

$$\frac{dC}{dt} = E(t)\frac{A_{contam}}{V} - C(t)\frac{Q}{V},$$

This equation can be simplified to Equation 3.

Equation 3

$$\frac{dC}{dt} = E(t)l - C(t)n\ ,$$

where

C(t)	= time dependent chamber vapor concentration (mg/m^3),
V	= chamber volume – test item volume (m^3),
Q	= air flow rate (m^3 min^{-1}),
A_{contam}	= contaminated surface area of test article (m^2),
E(t)	= time dependent emission factor of test article (mg m^{-2} min^{-1}),
l	= loading factor = A_{contam} / V (m^2/m^3),
n	= air change rate = Q / V (min^{-1}).

Calculate the Contaminated Surface Area: The contaminated surface area (A_{contam}) is calculated from the image analysis. It is recommended that the drop area immediately before decontamination begins is used as the contaminated area. For calculations used in the calculation of a vapor hazard, the term relative surface coverage (RSC) is defined as the ratio of the contaminated surface area to the total surface area of the coupon (A_{contam}/A_{coupon}). The images for the three CARC coupons are shown in Figure 7E-2. The coupon area and calculated RCS are listed in Table 7E-3.

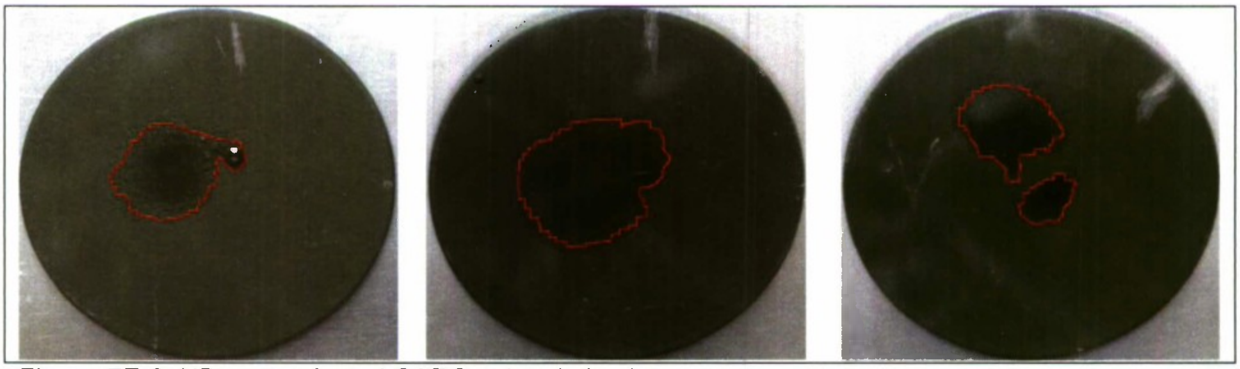

Figure 7E-2. HD contaminated CARC painted aluminum coupons.

Table 7E-3. Coupon contaminated area.

Vapor Chamber (number)	Coupon Area (cm^2)	Contaminated Surface Area (cm^2)	RSC (cm^2)
1	20.2	1.44	7.13
2	20.2	2.54	12.6
3	20.2	1.42	7.03

Calculate the Loading Factor: The loading factor is the ratio of contaminated surface area to the chamber volume and is calculated by Equation 4. The loading factor for the demonstration data set is calculated and presented in Table 7E-4. The reader should note that some of the data is presented in centimeters and results in meters; the appropriate conversions, not shown, should be performed as part of the data calculations. If the area is not directly measured, then the resulting emission factor should be noted as approximated as the loading factor calculated here is approximated.

Equation 4

$$l = \frac{A_{contam}}{V},$$

where

l = loading factor (m^2/m^3),

A_{contam} = contaminated surface area of test article (m^2),

V = chamber volume – test item volume (m^3).

Table 7E-4. Loading factors for demonstration test coupons

Vapor Chamber number	Contaminated Surface Area, A (cm^2) [m^2]	Vapor chamber Volume, V (m^3)	Loading Factor, l (m^2 / m^3)
1	1.44 [1.44×10^{-4}]	3.21×10^{-5}	4.49
2	2.54 [2.54×10^{-4}]	3.21×10^{-5}	7.91
3	1.42 [1.42×10^{-4}]	3.21×10^{-5}	4.39

Calculate the Air Change Rate: The calculation uses the chamber air flow rate and the chamber free air volume. The free air volume is determined by subtracting the volume of all 'solids' in the chamber such as the test article (i.e., coupon), mixing fans, or other solid structures from the chamber total volume. The air change rate *n* is calculated by as shown in Equation 5. The air exchange rates for the demonstration test coupons are presented in Table 7E-5.

Equation 5

$$n = \frac{Q}{V},$$

where

n = air change rate (min^{-1}),

Q = chamber air flow rate (mL min^{-1}),
V = chamber volume – test item volume (m^3).

Table 7E-5: Air change rates for demonstration test coupons

Vapor Chamber (number)	Air Flow Rate, Q (mL/min.)	Air Flow Rate, Q (m^3/min.)	Vapor chamber Volume (m^3)	Test Item Volume (m^3)	Open Chamber Volume, V (m^3)	Air Change Rate, I (min^{-1})
1	300	0.0003	3.85×10^{-5}	6.43×10^{-6}	3.21×10^{-5}	9.34
2	300	0.0003	3.85×10^{-5}	6.43×10^{-6}	3.21×10^{-5}	9.34
3	300	0.0003	3.85×10^{-5}	6.43×10^{-6}	3.21×10^{-5}	9.34

<u>Calculate the Emission Factor Directly</u>: The direct calculation of the emission factor as a function of time is given by Equation 6.

Equation 6

$$E(t_m) = \frac{\frac{\Delta C_m}{\Delta t_m} + nC_m}{l},$$

where ΔC/Δt is calculated using Equation 7.

Equation 7

$$\frac{\Delta C_m}{\Delta t_m} = \frac{\frac{C_m - C_{m-1}}{t_m - t_{m-1}} + \frac{C_{m+1} - C_m}{t_{m+1} - t_m}}{2},$$

where

$E(t_m)$ = the emission factor at time t_m (mg m^{-2} min^{-1}),
C_m = the vapor concentration at t_m (mg m^{-3}),
t_m = midpoint tube pull time for concentration measurement (min.).

Note that the calculation of ΔC/Δt for time t_m references time t_{m-1}, thus an emission factor cannot be calculated for the first concentration measurement. The same effect is generated for the last concentration measurement; because ΔC/Δt for time t_m references time t_{m+1}, the emission factor for the last concentration measurement cannot be calculated. This is source of the effect that if *x* chamber vapor concentrations are collected, *x*-2 emission factors can be calculated.

Advanced techniques can be used directly fit the differential equation, rather than using this direct calculation. If an advanced technique is used, the methods or software used should be documented in the test report. Report the emission factor, *E(t)* in units of mg m^{-2} min^{-1}, and the time for which the emission factor was calculated t_m (min.). The calculated emission factor,

vapor concentration and midpoint sample times shown in Table 7E-6 should be included as a report appendix to enable re-evaluation of the data if needed at a later time.

Table 7E-6. Calculated emission factor example

Vapor Chamber	Tube	Vapor Concentration C_i	Midpoint Sample Time, t_i	Concentration, Term, $C_\#$	Emission Factor, $E(t_m)$
(number)	(number)	(mg/m^3)	(min.)	(number)	($mg\ m^{-2} min^{-1}$)
1	0	0.001	0.0	C_0	N/C
1	1	0.743	7.5	C_1	$C_{0\ to\ 2}$ = 1.558
1	3	0.275	27.5	C_2	$C_{1\ to\ 3}$ = 0.572
1	4	0.179	75.0	C_3	$C_{2\ to\ 4}$ = 0.372
1	5	0.113	137.5	C_4	$C_{3\ to\ 5}$ = 0.236
1	6	0.073	330.0	C_5	N/C

4.0 Calculate the Emission Factor Model

The Emission Factor Model is an empirical model (i.e., equation) that represents the emission factors as a function of time. The emission factor model is required to calculate the vapor concentration that would be present in a specified scenario. The emission factor model is calculated by fitting an equation to the calculated emission factors. The emission factor should be calculated for each coupon. The emission factor model will use all replicates for a given test condition to determine the model. For example, if five coupons were treated identically through the decontamination process, the emission factor would be calculated for each coupon. This procedure would fit the data of all five coupons to produce one emission factor model. The emission factor model is also an ideal way to compare decontaminant test data as the results should be independent of test conditions and test chambers.

The emission factor will change as a function of time due to the various mass transport mechanisms of the contaminant in a given material and how the decontaminate neutralized or removed the contaminant. The physical mechanism that drives the mass transport could be evaporative, diffusion limited, or other mechanisms, and is highly dependent on the structure of the material and the material-agent interactions. There are many empirical models that can be used to fit the emission factor including, but not limited to:

Constant emission source model (Equation 8),

Equation 8

$$E(t) = A,$$

power law model (Equation 9),

Equation 9

$$E(t) = At^B,$$

first-order decay model (Equation 10),

Equation 10

$$E(t) = A\exp(-Bt),$$

Second-order decay model (Equation 11),

Equation 11

$$E(t) = \frac{E_0}{1 + ktE_0},$$

peak model (Equation 12),

Equation 12

$$E(t) = A\exp\left[-\frac{1}{2}\left(\frac{\log\left(\frac{t}{t_0}\right)}{2B}\right)^2\right],$$

A, B, E_0, k, and t_0 are the fitting coefficients (units vary by model). *t* is the time (min.). In most cases, it is expected that the first- or second-order decay will fit most materials, with the peak model possibly applying to some elastomers. If the calculated emission factor goes to zero, the first instance of this occurrence should be used in the data fitting, subsequent data points below detection should not be used for model fitting. The emission factor can be assigned to a value of zero for time points after the first occurrence of below detection.

Determine the Emission Factor Model: To determine the emission factor model, fit the emission factor data to the empirical models using an appropriate statistical tool such as Excel, Matlab, Sigma Plot. Using statistical parameters including the sum of the square of the error (SSE), root mean square error (RMSE), and R^2, evaluate and select the model that provides the best fit. The best fit will provide smaller SSE and RMSE values and an R^2 near 1.0. If no model presents a good fit to the data, the calculation of a scenario vapor concentration may be inaccurate.

Report the emission factor model used, the coefficients of the model, and the statistical parameters used to identify the model (e.g., SSE, RMSE, R^2). Provide a plot of the model with E(t) data points to visually display the fit to the data. The emission factor model should be reported in units of mg m^{-2} min^{-1}. For this data, the second order empirical model (Equation 11) provided the best fit with the parameters of E_0=1.862, k = 0.01735.

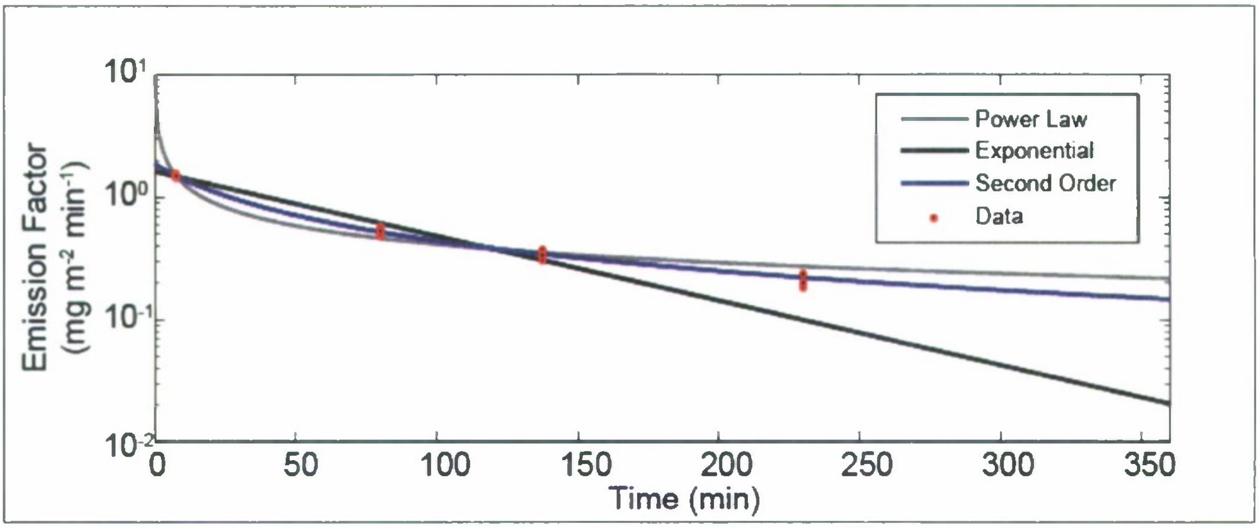

Figure 7E-3. Vapor test case study emission factor versus time plot.

Table 7E-7. Statistical analysis of emission factor models.

Parameter	Second Order	Exponential	Power Law
Equation	$E(t) = \dfrac{E_0}{1 + ktE_0}$	$E(t) = A\exp(-Bt)$	$E(t) = At^B$
Coefficient 1	E_0 = 1.862	A = 1.619	A = 4.114
Coefficient 2	k = 0.01735	B = 0.01213	B = -0.4993
SSE	0.01375	0.0720	0.04082
RMSE	0.03708	0.08485	0.06389
R^2	0.9956	0.9767	0.9868

5.0 Calculate the Scenario Concentration

The scenarios used to evaluate vapor test results should be agreed upon by the test sponsor to address the scenarios or interest to the sponsor or as specified in the requirement document for a specific acquisition program. This section contains some initial scenarios to demonstrate equation use and data evaluation. These scenarios are for teaching purposes only. The demonstration scenarios include an elevator, a conference room, an office, an auditorium and the cargo bays of a C5 and C141 aircraft.

The first step in the process is to identify several key parameters for the scenario of interest. Key parameters include the scenario total volume ($V_{S\text{-}T}$), the air flow rate and the air change rate. The scenario concentration calculation uses the free air volume for the scenario of interest. The free air volume is the total scenario volume minus the volume of the articles occupying the same space. The 1 m^2 standard panel is the most basic version of this calculation. For this case, the free air volume is the same as the scenario volume. The scenario concentration calculation for large items (e.g., vehicles in cargo bay) requires the determination of the occupied volume and the calculation of the free air volume.

The air exchange rate is needed for the scenario concentration calculation. The air exchange rate is calculated by

Equation 13

$$n_{scenario} = \frac{Q_{scenario}}{V_{scenario}}$$

If the scenario air change rate is specified, then the air flow rate does not need to be back calculated for the 1 m^2 panel calculation; however, for larger items or composite systems, the air flow rate must be calculated in order to calculate the air change rate for the scenario free volume. Also note that air change rate was, if specified by scenario, should be in units of 1/min. The sample scenario key parameters are provided in Table 7E-8.

Table 7E-8. Sample scenario dimensions, volume and air change rates for empty room

Scenario Name	Dimensions, l x w x h (m × m × m)	Room Volume, $V_{S\text{-}T}$ (m^3)	Air Flow Rate, $Q_{S\text{-}T}$ (m^3 / min.)	Air Change Rate, n (min^{-1}) [hr^{-1}]
Elevator[a]	1.5 × 1.5 × 3	6.75	0.6858	0.1016 [6.1]
Conference room[a]	10 × 5 × 3.5	175	15.23	0.0871 [5.23]
Office[a]	5 × 5 × 3.5	87.5	1.132	0.0129 [0.774]
Auditorium 180 seat[a]	46 × 26 × 10	11960	76.20	0.00637 [0.38]
C141 aircraft cargo bay[b]	28.5 × 3.05 × 2.74	86.45	N/C	0.333 [20]
C5 aircraft cargo bay[b]	37 × 5.8 × 4.1	879.9	N/C	0.333 [20]

[a]Air flow rates determined by ASHRAE standard 62-1999, Ventilation for acceptable indoor air quality specifying 1 cfm/ft^2 floor space for elevator and 20 cfm per person for commercial environments.
[b]aircraft cargo bays obtained from http://www.theaviationzone.com, air change rates for passenger cabins in Boeing aircraft as military air change rates were not readily accessible.

Specify the Relative Contamination Surface Coverage (RSC): The next step is to identify the surface area of the emitting item in the scenario. The default item area is a 1 m^2 'plate' of material into the scenario. Similar to the laboratory experiment, the entire surface of the item will not be contaminated with agent. For this reason the RSC of the item will be used to identify the contaminated surface area of the item (i.e., only the contaminated region of the item will be emitting vapor). The contaminated surface area is calculated by

$$A_{contam} = A_{item} \cdot RSC$$

If a known specific item is to be placed in the scenario, the surface area of that item should be used. For example, if a vehicle was to be the contaminated item and this was testing the emission of CARC, the total surface area of CARC on the vehicle should be used for A_{item}. The use of a default 1 m^2 item area is used as a guide to enable comparison between data.

This calculation should be performed for multiple RSC including, the mean relative surface coverage observed during testing, and several specified RSC. In cases where different laboratories performed the test and observed different RSC, the 'as tested' case will produce vapor concentrations that will likely be different (larger surface coverage generating larger vapor concentrations). However, for the case where the relative surface coverage is specified (e.g., 10% coverage) it is likely that the scenario vapor concentrations will be similar. Table 7E-9

contains example RSC to demonstrate the scenario calculation. These coverages are not from an approved list.

Table 7E-9. Example scenario suggested relative surface coverage values.

Scenario, A_{item}	Example Suggested RSC	A_{contam}
1 m^2 (default)	test mean, example 0.05	0.05 m^2
1 m^2 (default)	0.07 (default RSC for 1 g/m^2 test)	0.07 m^2
1 m^2 (default)	0.30 (default RSC for 10 g/m^2 test)	0.30 m^2

Calculate the Loading Factor: The scenario loading factor, $l_{scenario}$, is calculated by Equation 14.

Equation 14

$$l_{scenario} = \frac{A_{contam}}{V_{scenario}}$$

Calculate the Scenario Vapor Concentration: Calculating the scenario vapor concentration requires scaling the small-scale dynamic vapor chamber data to a 'real world' scenario. The mathematics to perform this operation are well established. However, care must be taken to accurately account for and recognize the assumptions and limitations of the models used to calculate the vapor concentrations. The vapor hazard is calculated by determining the scenario vapor concentration as a function of time, then calculating the toxic load associated with the vapor concentration profile. The toxic load can be compared to requirements and toxicology data to determine if the scenario is 'safe.'

The desired accuracy of the vapor concentration in a scenario determines the amount and type of test data to be acquired, in addition to the level of modeling applied in the scale up calculation. Essentially, higher accuracy scaling requires considerable computational power and complex models such as computed flow dynamics (CFD). Due to the cost of the software, hardware and expertise required to perform such modeling, in addition to the number of scenarios and volume of data that could be generated in this type of evaluation it is not reasonable perform modeling on the CFD level of detail. Because this procedure is designed for decontamination evaluation rather than providing a detailed simulation, a simple model is provided to give an approximate representation of the vapor concentration that would be encountered in a real world scenario. This calculation will determine the scenario vapor concentration. The following assumptions are made:

- The emission factor model data was collected for a time period equal to or longer than the scenario duration. Time extrapolation of the emission factor model is not safe.
    - Caveat – if the emission factor is determined to diminish to a zero value, zeros can be extrapolated in time provided residual agent measurements indicate no residual agent.
- The initial vapor concentration in a scenario is assigned to C(t=0) = 0 mg/m^3; the initial environment is 'clean.' The initial concentration could be set to any other value if needed.
- If the mass transport mechanism is evaporative these calculations do not account for the effect of air velocity, or concentration gradients that may affect the emission factor. Test conditions (air velocity) should match the scenario to ensure proper scaling of evaporative emission.

- The following calculations apply to enclosed volumes ('indoor' environments), modeling outdoor environments requires dispersion models (e.g., SCIPUFF, VLSTRACK, CFD).
- The enclosed volume is well mixed.
- The presented model does not account for 'sinks' that will exists in real world scenarios that would absorb vapor and decrease the actual vapor concentration.
- The model does not account for changes in emission factors as a function of temperature – scenario temperature is the same as the temperature the test data was generated.

This equation is solved numerically by calculating the concentration for discrete time steps, Δt. It is recommended that the time step interval, Δt, value is 0.1 min (if erratic vapor concentrations are observed smaller Δt values should be used). The initial concentration C(t=0) should be set to 0 mg/m^3. The calculation should be carried out for the duration of a scenario.

Equation 15

$$C_S(t) = E(t) l_{scenario} \Delta t - C(t - \Delta t) n_{scenario} \Delta t + C(t - \Delta t)$$

Where:

$C_s(t)$	= vapor concentration for the scenario at time t (mg/m^3),
C(t-□Δt)	= vapor concentration for the scenario at the previous time step value t-□Δt (mg/m^3),
t	= current time step (min.),
Δt	= time step increment (min.),
E(t)	= emission factor model for the material (mg m^{-2} min^{-1}),
$n_{scenario}$	= scenario air change rate (min^{-1}),
$l_{scenario}$	= scenario loading factor (m^2 / m^3),

Plot the calculated $C_s(t)$ as a function of time, as shown in Figure 7E-4. This corresponds to the vapor concentration to which unprotected personnel in the scenario would be exposed. An example calculation including vapor concentration and toxic load are provided later in the text in Table 7E-12.

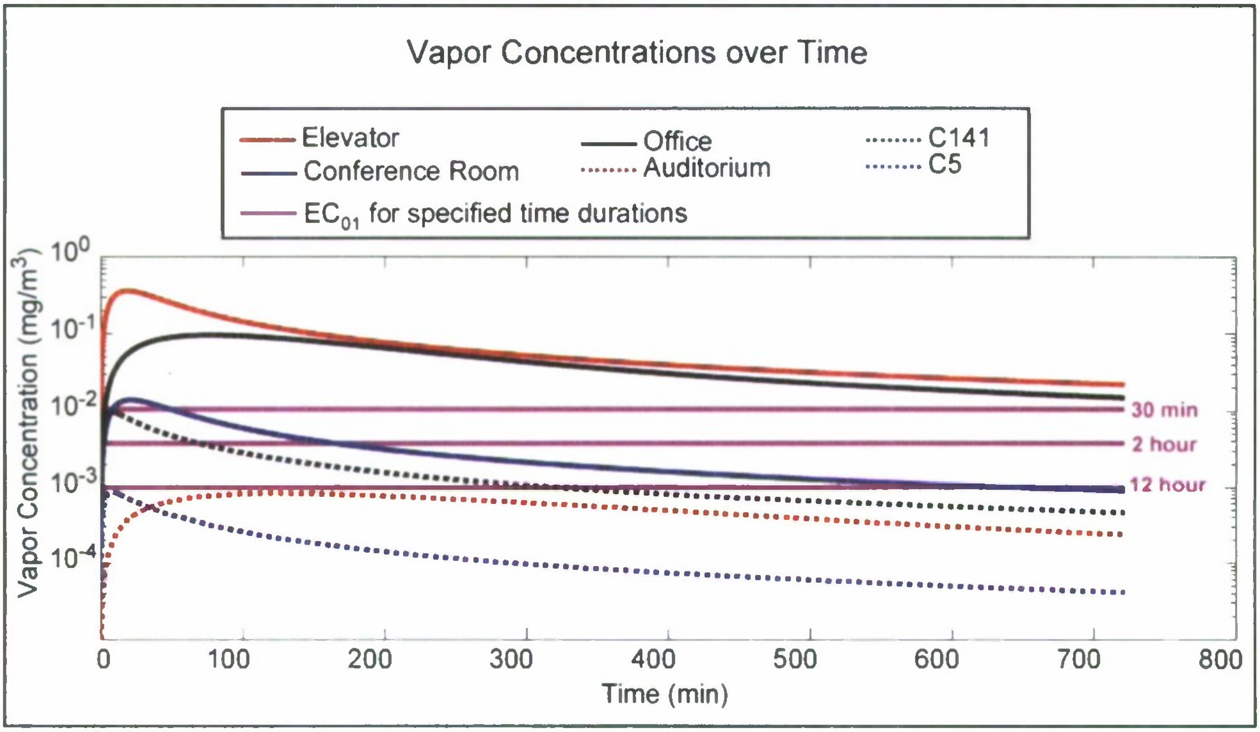

Figure 7E-4: Vapor test scenario vapor concentrations plotted vs. time.

6.0 Calculate the Toxic Load

To establish if a given scenario vapor concentration is safe for unprotected personnel, the toxic load is calculated. Historically, time weighted average vapor concentrations were used to compare to a requirement to determine if a scenario was safe. Guidance from toxicology experts and FM 3-11.9 suggest the use of calculating an exposure using a toxic load (TL) model to determine if a scenario is safe.

Toxic Load Exponent: To calculate a toxic load exposure, the toxic load exponent must be selected. The typical variable used to describe the toxic load exponent is, n, not to be confused with the air change rage using the same variable name. The toxic load exponent is a function of the agent and can be found in FM 3-11.9, current values are presented in Table 7E-10. In recent documents, various organizations have used different toxic load exponents. Decontamination testing should compare use the toxic load exponents for mild effects which are identified using yellow highlighter in Table 7E-10. For example, if the data corresponds to the agent GD, a toxic load exponent of n = 1.4 is selected.

Table 7E-10. Toxic load exponents used by FM 3-11.9 and by CHPPM to generate requirements

Route of Exposure	Effect	GD		VX		HD	
		FM 3-11.9	CHPPM	FM 3-11.9	CHPPM	FM 3-11.9	CHPPM
IH/OC	Lethal	1.25	2	1	2	1.5	1
IH/OC	Severe	1.25	2	1	2	1	1
IH/OC	Mild	1.4	2	1	2	1	1
PC	Lethal	1	N/A	1	N/A	1	N/A
PC	Severe	1	N/A	1	N/A	1	N/A
PC	Mild	1	N/A	1	N/A	1	N/A

IH/OC – inhalation/ocular exposure
PC – percutaneous (through the skin)
yellow highlighter indicates the value that should be used for toxic load calculations in this report.

Scenario Toxic Load Calculation: The toxic load, *TL*, for a scenario is calculated using the scenario vapor concentration, $C_S(t)$. This calculation will generate a single number that can be compared to a requirement to determine if a scenario would induce a toxicological response. The toxic load is calculated using the ten Berge equation (Equation 16)

Equation 16

$$TL = \int C_S(t)^n \, dt .$$

Because the vapor concentration was calculated numerically using discrete time steps, the toxic load for any time duration from t_{start} to t_{end} is expressed as the summation shown in Equation 17

Equation 17

$$TL = \sum_{t_{start}}^{t_{end}} C_S(t)^n \cdot \Delta t ,$$

Using a notation similar to the numerical method to calculate the vapor concentration and setting the boundary conditions of $t_{start} = 0$ and $TL(t_{start}) = 0$, the toxic load can be calculated as shown in Equation 18

Equation 18

$$TL(t) = TL(t - \Delta t) + C_S(t)^n \Delta t ,$$

where

$TL(t)$ = toxic load at time t (mg^n min./m^{3n}) – note units vary with *n*,

$TL(t-\Delta t)$= toxic load at the previous time step,

$C_S(t)$ = scenario vapor concentration at time t (mg/m^3),

n = toxic load exponent (unitless),

t_{start} = integration start time (min.),

t_{end} = integration end time (min.),

Δt = time step size (min.).

The end time should correspond to the scenario duration ($t_{scenario}$). The time step size, Δt, must be the same as that used to calculate the scenario vapor concentration. The quantity $C_S(t)^n \Delta t$ corresponds to the toxic load exposure for a time step, Δt. The toxic load value for the scenario duration, $TL(t_{scenario})$, should be compared to a requirement value. The calculation of $C_S(t)$ and TL(t) is illustrated in Table 7E-11 for the elevator scenario. The results of the same calculation for all of the listed scenarios are provided in Table 7E-12.

Table 7E-11. Sample calculation of the elevator scenario for GD, with n = 1.4.

Time (min.)	**E(t)**[a] (mg m^{-2} $min.^{-1}$)	**C_S(t)** (mg/m^3)	**$C(t)^n\Delta t$** ($mg^{1.4}$ min. $m^{4.2}$)	**TL(t)** ($mg^{1.4}$ min. $m^{4.2}$)
0.0[b]	1.862	0.00[b]	0.00	0.00[b]
0.1	1.856	0.0041	4.58×10^{-05}	4.58×10^{-05}
0.2	1.850	0.0082	1.20×10^{-04}	1.66×10^{-04}
0.3	1.844	0.0122	2.09×10^{-04}	3.75×10^{-04}
0.4	1.838	0.0162	3.10×10^{-04}	6.85×10^{-04}
0.5	1.832	0.0201	4.20×10^{-04}	1.10×10^{-03}
0.6	1.827	0.0239	5.37×10^{-04}	1.64×10^{-03}
0.7	1.821	0.0277	6.60×10^{-04}	2.30×10^{-03}
0.8	1.815	0.0315	7.88×10^{-04}	3.09×10^{-03}
0.9	1.809	0.0351	9.21×10^{-04}	4.01×10^{-03}
1.0	1.804	0.0388	1.06×10^{-03}	5.07×10^{-03}
. . .	. . .	. . .	. . .	. . .
720.0	0.0768	0.0169	3.31×10^{-04}	15.2

[a] E(t) is calculated using the equation $E(t) = E_0 / (1+E_0kt)$ derived in Section 4.

[b] The values t_{start}, $C(t_{start})$, and $TL(t_{start})$ were set by the boundary conditions.

Table 7E-12. Scenario descriptions and toxic load values for a 12 hour (720 min.) duration.

Scenario	**Contam. Surface Area** (m^2)	**Volume** (m^3)	**Air Change** ($min.^{-1}$)	**Loading Factor** (m^2/m^3)	**TL (0 to 12 hr)** ($mg^{1.4}$ min. $m^{4.2}$)
Elevator	0.15	6.75	0.102	0.0222	15.2
Conference Room	0.15	175	0.0871	0.000857	0.198
Office	0.15	87.5	0.0129	0.00171	6.55
Auditorium	0.15	11960	0.00637	0.0000130	0.0158
C141	0.15	86.5	0.333	0.00174	0.0836
C5	0.15	880	0.333	0.000170	0.00325

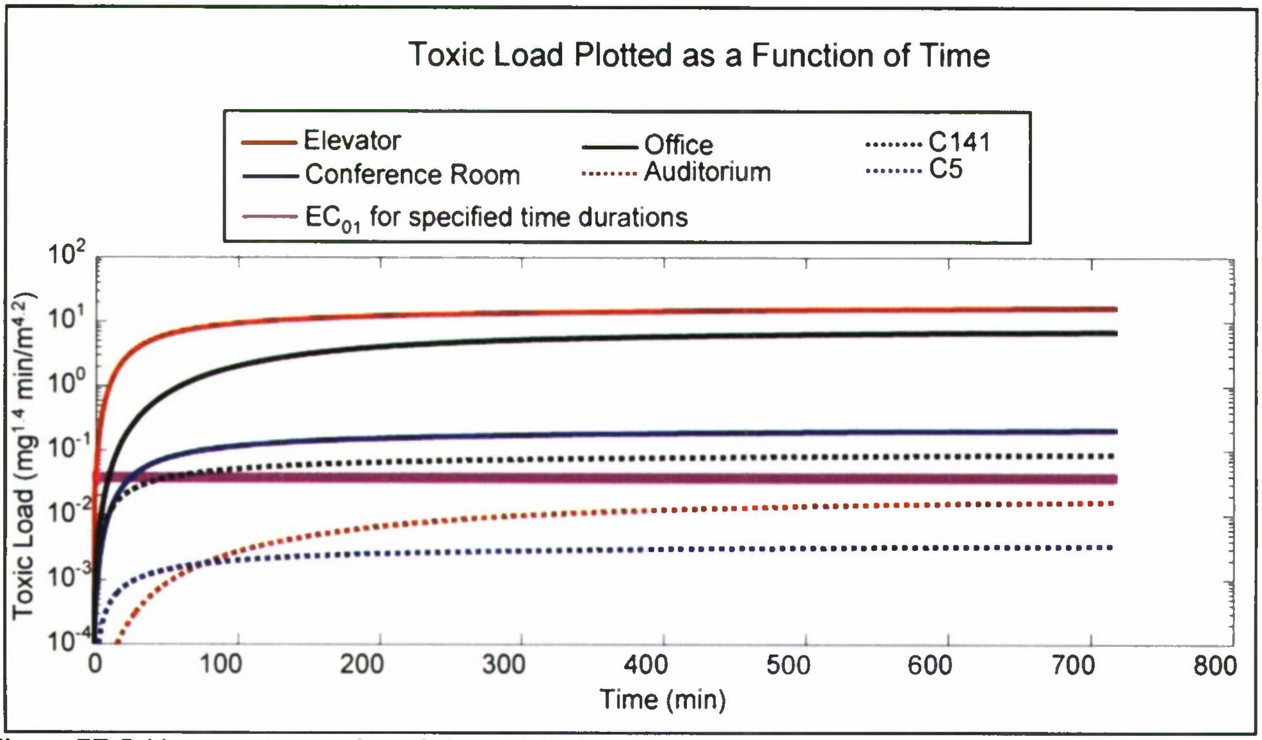

Figure 7E-5. Vapor test scenario toxic load plotted vs. time.

Scenario and Toxicological Toxic Load Comparison: The toxic load can be compared to a requirement to determine if a toxicological response will be observed. FM 3-11.9 lists toxic load exposures that would induce a response in 50% of the population. Table 7E-13 uses extrapolations that correspond to toxic load exposures that would induce a response in 16 percent (ETL_{16}) or 1 percent (ETL_{01}) of the military population. The 1 and 16 percent population values are often used to generate requirements. If the calculated TL value is greater than the value listed in Table 7E-13, then a toxicological response will be observed for the corresponding population percentage.

Table 7E-13. Toxic load values for common tested agents

Agent	**HD & L**			**VX**		
Toxic Load Exponent	n = 1			n = 1		
Effects	Mild (eye irritation)			Mild (miosis, rhinorrhea)		
Units	mg min./m^3			mg min./m^3		
Level	ETL_{50}	ETL_{16}	ETL_{01}	ETL_{50}	ETL_{16}	ETL_{01}
Toxic Load	25.0	11.6	4.2	0.1	0.056	0.026

Agent	**GD & GF**			**GA & GB**		
Toxic Load Exponent	n = 1.4			n = 1.5		
Effects	Mild (miosis, rhinorrhea)			Mild (miosis, rhinorrhea)		
Units	mg$^{1.4}$ min./m$^{4.2}$			mg$^{1.5}$ min./m$^{4.5}$		
Level	ETL_{50}	ETL_{16}	ETL_{01}	ETL_{50}	ETL_{16}	ETL_{01}
Toxic Load	0.0796	0.0572	0.0371	0.179	0.128	0.0831

7.0 Scientific Discussion and Reporting Guidance

Prior comparisons of vapor data to requirements were often binary approaches evaluating if a decontaminant met a requirement value. In many cases this binary comparison was made using different data treatment approaches. In addition, vapor hazard is scenario dependent. The lack of sufficient information from requirements limited the ability to correctly calculate for the scenario. The binary data evaluation approach did not provide proper guidance for decontaminant development. The data analysis method did not provide context (e.g., scenario) or proper utilization (e.g., toxicological effects). The approach of this method update has been to build a foundation to compare test results to toxicological values and account for how scenario affects the hazard. The approach in this section is to use scenario vapor concentration profiles to determine the scenarios for which a hazard is present, a hazard is not present and when trade space considerations may exist. These curves can also identify when detectors may alarm. The toxic load values and curves determine if the material or item in the scenario poses a vapor hazard to unprotected personnel by comparison to a toxicological value. The examples in this section compare to the toxic load value for which 1% of the population would experience a toxicological response. All of the scenarios shown in this section are based on a 12 hour mission length.

This type of data analysis is best suited for later R&D and field testing to determine potential applicability to an acquisition program. Early decontaminant evaluations should focus on the removal of as much contaminant as possible. Later R&D activities should assess the hazard the remaining agent creates. This type of testing and data analysis does not replace the need for later DT/OT testing on actual items using the final applicator system and decontaminant process. This analysis is meant to enhance the overall research, development and testing process.

<u>Vapor Concentration Profiles</u>: The vapor concentration profiles provide guidance regarding the decontaminant treatment performance for the reduction of agent contamination on and in the material of interest. The 12 hour EC_{01} for GD is 0.00087 mg/m^3. This value is shown in Figure 7E- using a thick, pink dividing line labeled 12 hour. The scenarios fall into three groups for concentration profiles that remain above (a), cross (b) and remain below (c) the 12 hr dividing line. The results are discussed further in the bulleted list.

- Group (a): The elevator and office scenarios have vapor concentration above the dividing line for the entire 12 hr time period. These scenarios are expected to yield high toxic load values and result in a hazard to unprotected personnel. The decontaminant treatment performance was not sufficient for the material placed in these scenarios.
- Group (b): The conference room and C141 cargo bay scenarios have vapor concentrations that cross the dividing line over the course of the 12 hr period. It is not possible to determine the hazard to unprotected personnel solely from the concentration chart. The toxic load values must be considered. The conference room and C141 cargo bay scenarios identify a potential trade space to determine when the scenario may be safe for unprotected personnel.
- Group (c): The auditorium and C5 cargo bay have vapor concentrations below the dividing line for the entire 12 hr period. These scenarios are expected to yield low toxic load values and result in a scenario that is safe for unprotected personnel. The decontaminant treatment performance was sufficient for the material placed in these scenarios.

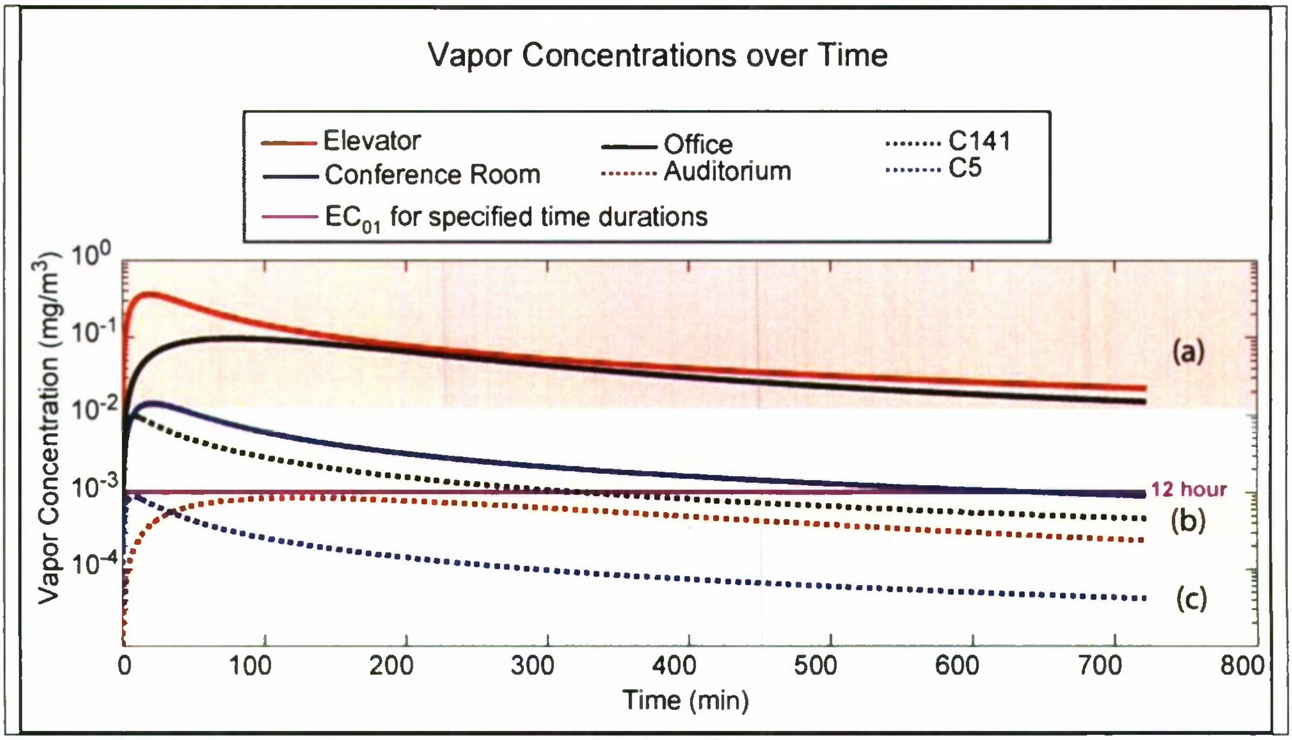

Figure 7E-6: Scenario vapor concentrations as a function of time.

Toxic Load: The toxic load value should be used to determine the hazard to unprotected personnel. The ETL_{01} for GD is 0.0371 $mg^{1.4}$ min / $m^{4.2}$ and is denoted in Figure 7E-7 using pink color text. The calculated toxic load values for the decontaminated material in the scenarios are shown in Figure 7E-7. The auditorium and C5 cargo bay scenarios toxic load values are well below the ETL_{01} for GD. The conclusion for these scenarios based on the experimental test data is that the decontaminant treatment was effective for this 1 m^2 decontaminated panel and that a vapor hazard is not present. The same decontaminated material placed in the elevator and office, however, poses a significant vapor hazard to unprotected personnel. The calculated toxic load values are significantly greater than the ETL_{01} for GD. The C141 cargo bay and conference room scenario calculated toxic load values are greater than the ETL_{01} for GD. The decontaminant treatment was not effective for these scenarios and a vapor hazard to unprotected personnel is present but not as severe as the elevator and office scenarios.

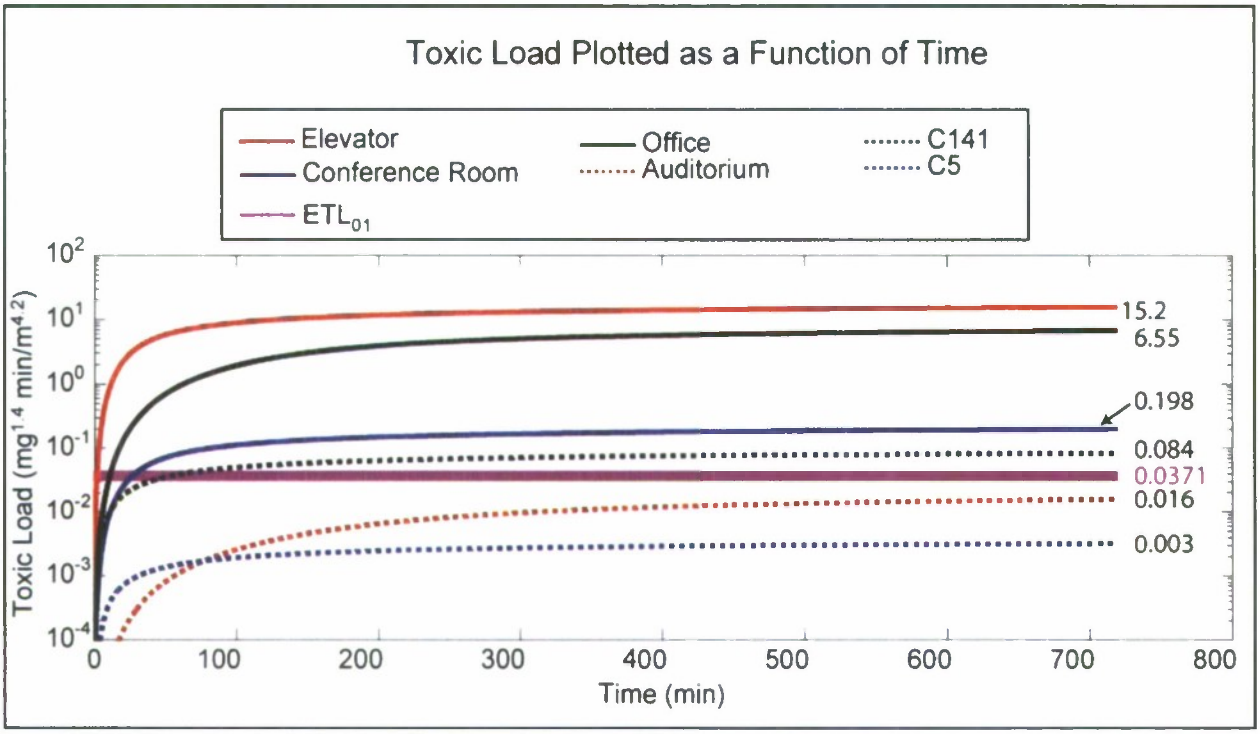

Figure7E-7: Scenario toxic load plotted as a function of time.

Trade Space: The scenario based evaluation offers greater context to the evaluation of decontaminant performance. The decontaminant treatment can be analyzed to determine the trade space for the decontaminant tested. This ability for trade space is evident for the C141 cargo bay and conference room scenarios. The C141 cargo bay demonstrated a toxic load of 0.056 $mg^{1.4}$ min / $m^{4.2}$ which is above 0.0371 $mg^{1.4}$ min. / $m^{4.2}$, the ETL_{01} for GD; however, this value is slightly below the ETL_{16} for GD listed in Table 7E-14. If it is acceptable for an operation to have up to 16% of the unprotected personnel affected in order to complete the mission, then this decontaminant performance may be reasonable 1 m^2 decontaminated panel in this scenario.

The majority of the toxic load for the conference room and C141 scenarios occurred during the first 3 hr post decontamination treatment. If the material could be placed elsewhere to offgas for three hours prior to being brought into the scenario, then the resulting toxic load would be below the ETL_{01} for GD for the C141 scenario (Figure 7E-8). If the material or contamination source could not be placed elsewhere, then the personnel would require protection until the safe level was achieved.

The ability to evaluate decontaminant performance across scenarios enables the researcher to greater opportunity to provide scientific meaning to decision makers. The vapor analysis can be used in conjunction with other information such as material compatibility. The vapor data evaluation may identify materials that may pose decontamination challenge compared to other materials. Improving the decontaminant to treat all the materials of interest may begin to affect material compatibility for materials with low vapor hazard. The ability to correlate the performance may suggest applications for which the decontaminant is effective but would require replacement of some materials if contaminated. A common example is silicone compared to metal, glass and CARC. A decision maker may choose that it is not worth

affecting the material integrity of the metal, glass or CARC if a decontaminant treatment posed no vapor hazard if the silicone was replaced.

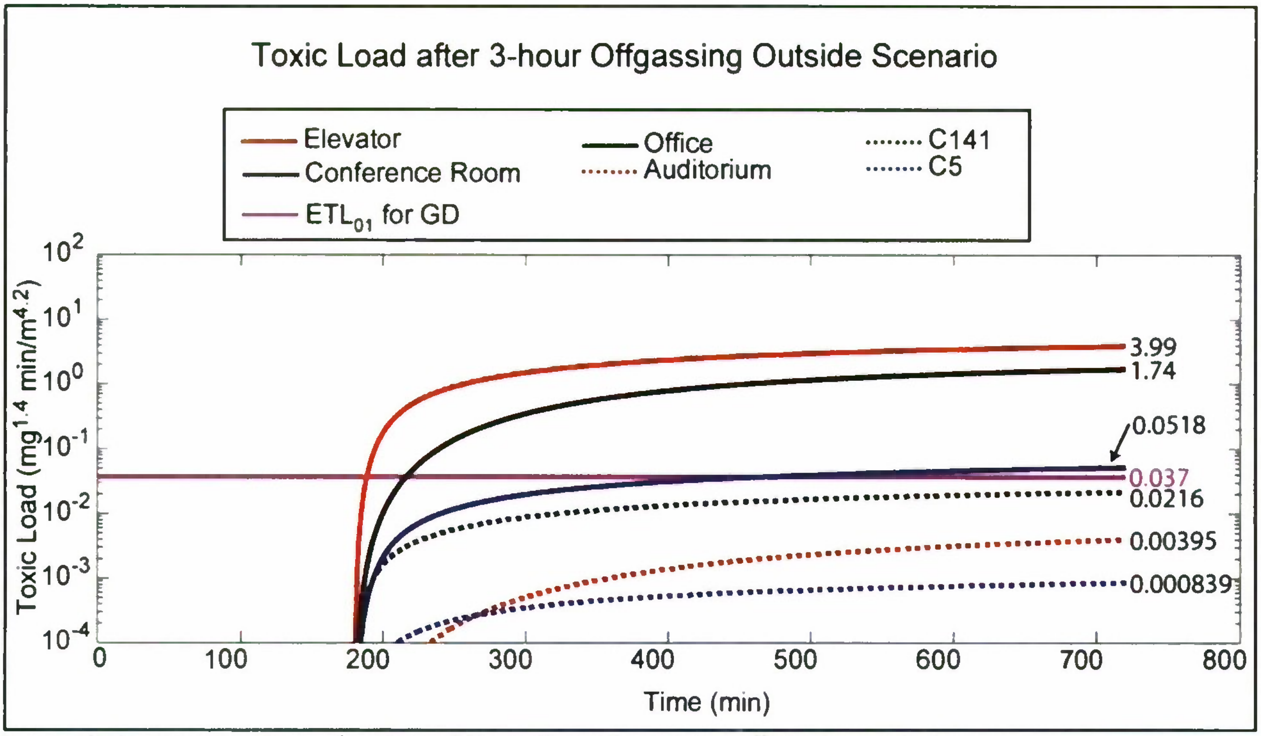

Figure 7E-8: Toxic load as a function of time after a three hour offgassing period.

Table 7E-14. Toxic load values for scenarios after a three hour offgassing period.

Scenario	**Contam. Surface Area**	**Volume**	**Air Change**	**Loading Factor**	**TL**[a]
	(m^2)	(m^3)	(min^{-1})	(m^2/m^3)	($mg^{1.4}$ min $m^{4.2}$)
Elevator	0.15	6.75	0.102	0.0222	3.99
Conference Room	0.15	175	0.0871	0.000857	0.0518
Office	0.15	87.5	0.0129	0.00171	1.74
Auditorium	0.15	11960	0.006370	0.000013	0.00395
C141	0.15	86.5	0.333	0.00174	0.0216
C5	0.15	880	0.333	0.000170	0.000839

[a]3 to 12 hour calculation after allowing item to aerate "outside" of scenario for 180 min.

Impact of Considering Single Material Data Alone: Vehicles, aircraft, buildings and equipment are constructed from multiple materials. The vapor data treatment during the later decontaminant development timeline should begin to factor in composite systems. A decontaminant may reduce the agent contamination on each material such that a vapor hazard does not exist to unprotected personnel. When the materials are then combined to create an item, such as a vehicle, the combine emission factors from the multiple materials may result in a

vapor hazard to unprotected personnel.

The multiple item vapor emission scenario should also be considered as applicable to the mission profile under evaluation. Figure 7E-9 shows a representation of the multiple item scenario. A laptop may have been directly tested or approximated from multiple material test data. The single laptop in the scenario of interest was below the ETL_{01} for GD is 0.0371 $mg^{1.4}$ min / $m^{4.2}$. If this scenario was a the decontamination of small items of sensitive equipment for personnel that once reissued would get into a large vehicle interior for transport, the combination of the items should be considered to determine if a the new scenario creates a risk to unprotected personnel. Using this example, if four or more laptops were placed into the vehicle, a vapor hazard is present to unprotected personnel.

The multiple material and multiple item scenarios reinforce the need to first reduce the total amount of agent in and on the material during early R&D and then evaluate the field procedures during later development to determine situations that may result in the creation of a secondary hazard.

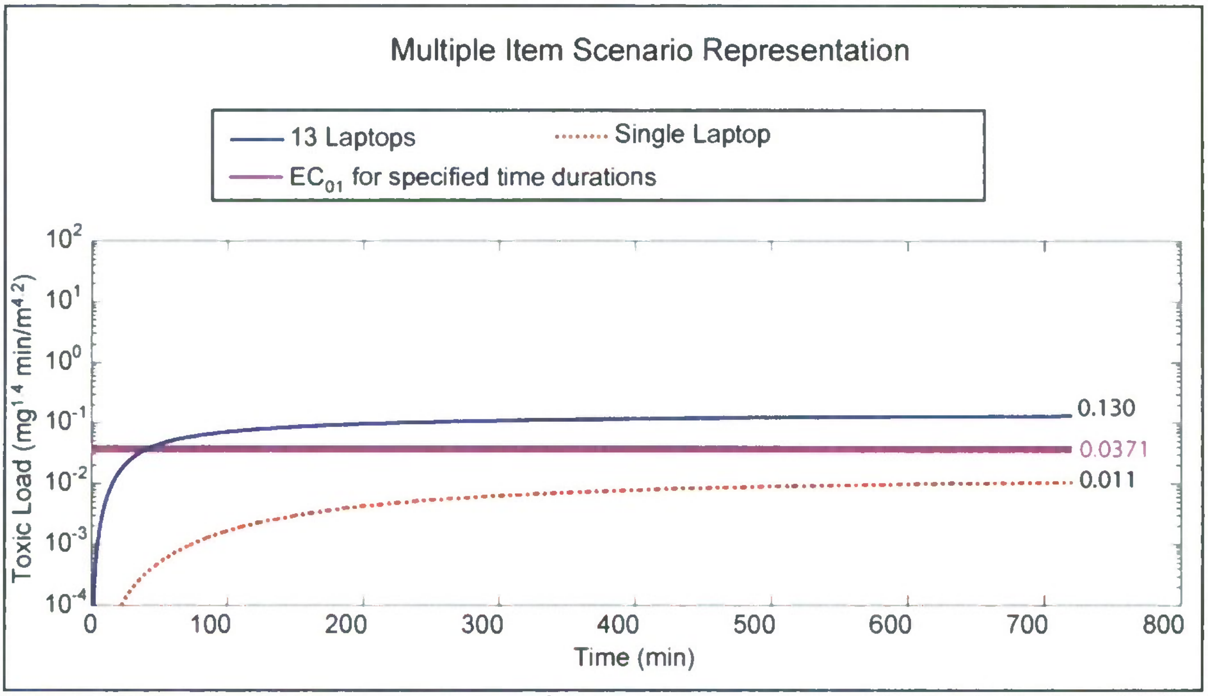

Figure 7E-9: Toxic load for multiple items as a function of time.

<u>Impact of Reporting TWA Instead of Toxic Load</u>: In some cases, reporting the time weighted average (TWA) instead of the toxic load can give a false impression that a vapor hazard does not exist. The TWA calculation method should not be used to determine if a vapor hazard exists for agents with a toxic load exponent not equal to one. The scenario Table 7E-15 shows the toxic load and TWA calculated results for the six scenarios. In these cases the TWA versus toxic load impact is not as dramatic. An example showing a dramatic difference is included in the corresponding vapor methodology development technical report.

Table 7E-15. Toxic load calculated results compared to TWA calculation

Scenario	Contam. Surface Area	Volume	Air Change	Loading Factor	TL (0 to 12 hr)	TWA (12 hour)
	(m^2)	(m^3)	(min^{-1})	(m^2/m^3)	($mg^{1.4}$ min $m^{4.2}$)	(mg/m^3)
Requirement	N/A	N/A	N/A	N/A	**0.0371**	**0.00087**
Elevator	0.15	6.75	0.102	0.0222	15.2	0.0556
Conference Room	0.15	175	0.0871	0.000857	0.198	0.00250
Office	0.15	87.5	0.0129	0.001714	6.55	0.0327
Auditorium	0.15	11960	0.00637	0.000013	0.0158	0.000456
C141	0.15	86.5	0.333	0.001735	0.0836	0.00132
C5	0.15	880	0.333	0.000170	0.00325	0.000130

Impact of Reporting Vapor Chamber as Scenario: Common practice was to determine vapor hazard based on the vapor emission from a test material in a small vapor chamber. This practice resulted in the inability to compare lab-to-lab data and raised questions regarding lab data utility when compared to field data. The vapor test chamber is a scenario. If the same calculation to generate the vapor concentration and toxic load profiles was performed for the vapor chamber used the result compared to the six scenarios is a significantly higher vapor concentration (Figure 7E-9) and toxic load (Figure 7E-10). Requiring R&D to develop decontamination technologies to result in no vapor hazard for the vapor chamber scenario could result in increased time, logistical burden and potential material incompatibility than would be required to adequately decontaminate the items of interest. The use of scenario based evaluations can better guide R&D efforts.

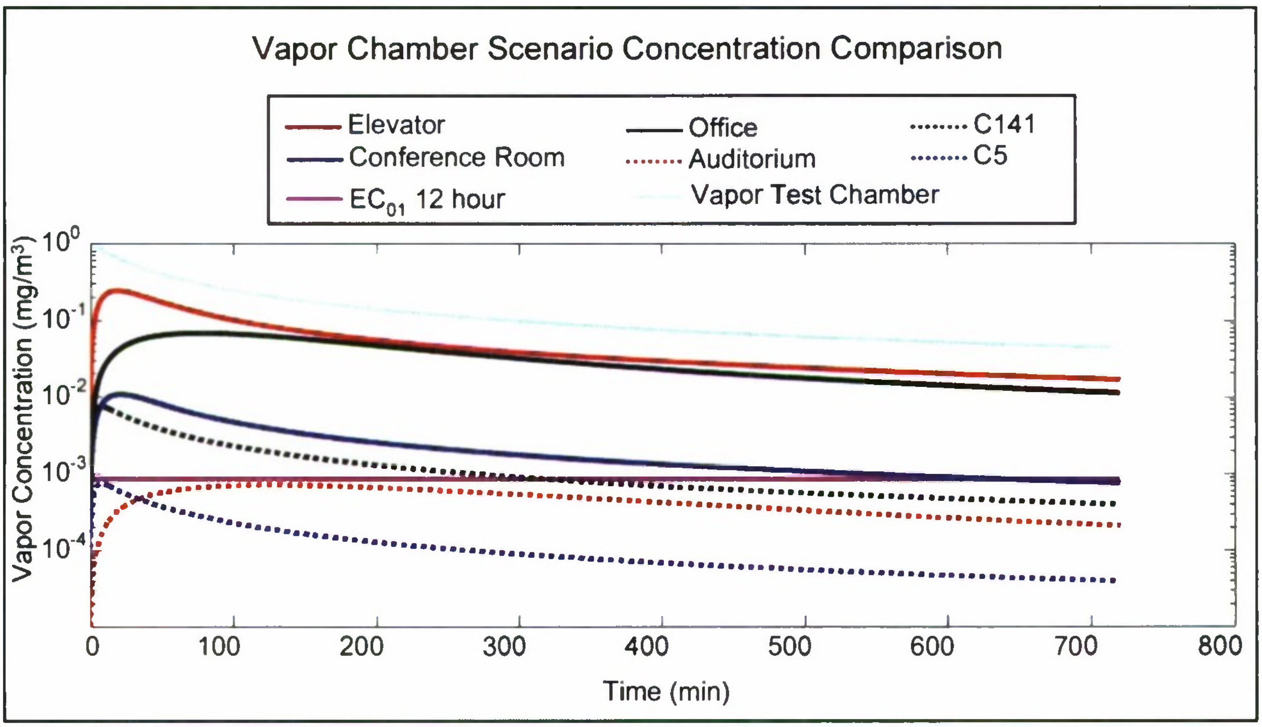

Figure 7E-9: Test chamber versus scenario vapor concentrations.

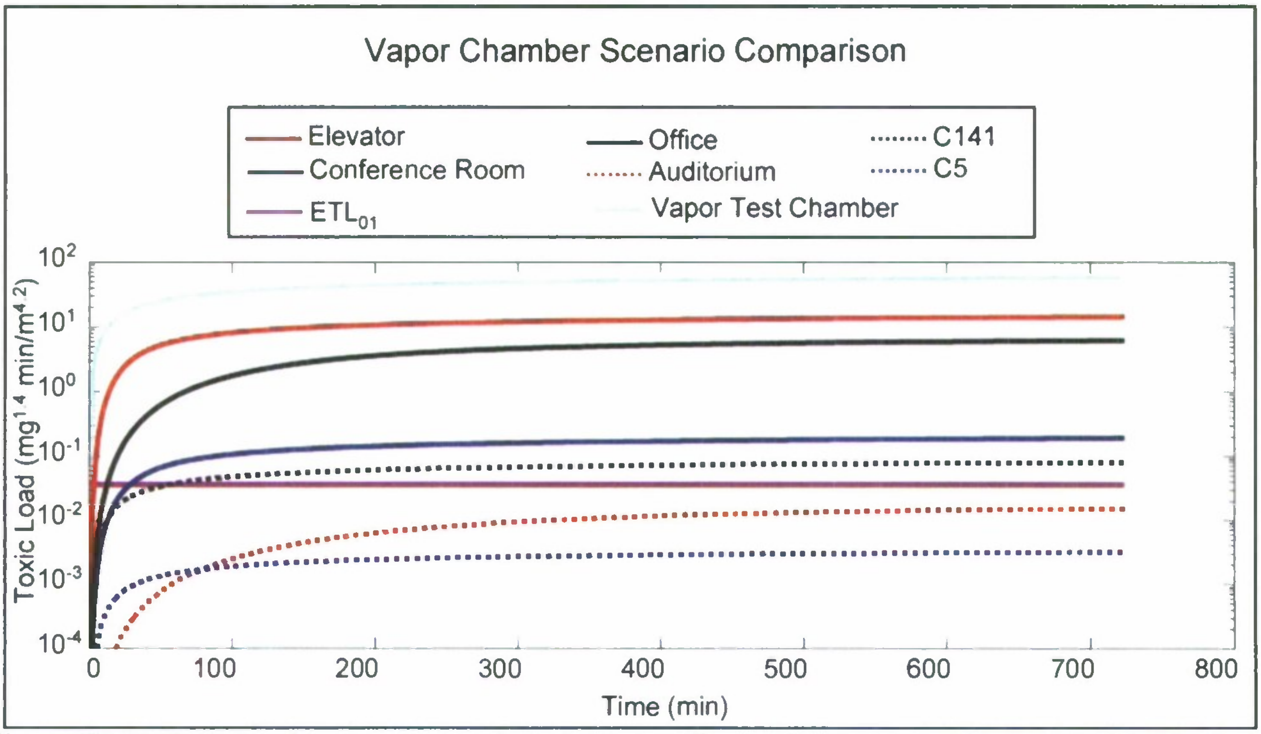

Figure 7E-10: Test chamber versus scenario toxic load profiles.

Table 7E-16: Test chamber versus scenario toxic load results.

Scenario	Air Change	Loading Factor	Contam. Surface Area	Volume	TL (0 to 12 hr)
	(min^{-1})	(m^2/m^3)	(m^2)	(m^3)	($mg^{1.4}$ min $m^{4.2}$)
Elevator	0.102	0.0222	0.15	6.75	15.2
Conference Room	0.0871	0.000857	0.15	175.0	0.198
Office	0.0129	0.001714	0.15	87.5	6.55
Auditorium	0.006370	0.000013	0.15	11960.0	0.0158
C141	0.333	0.001735	0.15	86.45	0.0836
C5	0.333	0.000170	0.15	879.9	0.00325
Vapor Chamber	7.79	4.50	0.000171	0.000038	61.7

REVISION HISTORY

March 2008: original method.

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Test Procedure 7-F: Chromatographic Analysis Guidance

SUMMARY

Program CA06DEC407 was a DTRA funded effort designed to address the challenges associated with quantifying low-level residual agent to support decontaminant contact- and vapor-test evaluations. The program had three main objectives.

- The primary program objective was to develop improved analytical methods to enable the confident detection of low-level of chemical agents VX, HD and GD at published requirement levels for testing using the 2-in. diameter circular coupons.
  - The lowest requirements at the time of this program used to establish the required detection limits were the Joint Platform Interior Decontamination (JPID) program 2003 and the Joint Service Sensitive Equipment Decontamination (JSSED) program 2005 requirement documents.
- The secondary program objective was to establish methods for the detection of common agent byproducts that could form during decontaminant testing.
- The tertiary program objective was to make the new methods available to establish uniformity in test procedures across testing locations.

The methods were written for analysis using mass selective detectors. Mass selective detectors were selected to increase confidence that the reported data was for the analyte of interest and not an interferent, product or other analyte. Other detection methods can be used, though mass selective detectors are recommended. The methods are formally documented in Appendix C. Each method is documented as an individual method. The methods are constructed using standardized fields with all pertinent information. The 'Analyte Concentration Range' section provides an overview of the method target, the calibration range, calibration curve fitting model and weighting, limit of detection (LOD), limit of quantitation (LOQ), solvent and quantitation ion(s). The methods are identified as quantitative or qualitative. The secondary program objective was byproduct identification. The byproduct methods as presented are qualitative. All qualitative methods in this document can be quantitative if a set of calibration standards of the byproduct are prepared and analyzed. The LOD and LOQ are calculated based on the laboratory evaluation of the final method. Each laboratory should recalculate these values based on their method performance. LOD and LOQ are a function of instrument sensitivity which can decay over time/use. Instrument sensitivity can often be restored by regular scheduled maintenance, thus illustrating the need for a regular maintenance schedule. It is anticipated that a laboratory can achieve the appearance of a better LOD and LOQ, especially for new equipment or following instrument maintenance. These values should be calculated over a period of time to determine the laboratory performance. The "Apparatus" section details the analytical equipment and standard preparation tools. The "Method Parameters" section provides the complete listing of instrumentation settings for the method.

The methods are established on the instrumentation software and configurations described in this document. These parameters may be used on similar or other GC/MS and/or LC/MS platforms and are comprehensive enough to serve as a guide for establishing low-level methods. Methods transferred to instruments set-up as described should obtain similar results; however, parameters applied to instrumentation different than described may not produce the same results. Method check-out must be performed, to include analyzing solvent blanks, chemical agent standards and by-product standards to verify instrument specific performance and method optimization. Table 7F-1 contains a summary listing of the agent, by-product, concentration range and corresponding analytical method for analysis. The method limits of detection and quantitation determined through the method development are also document.

Each lab using these methods is encouraged to determine their laboratory performance for the methods used to support decontaminant performance evaluations.

Table 7F-1. Analytical method listing.

Method listing for liquid extract samples.

Compound	Range	Method Name	Appendix Method
VX	0.05 – 10 ng/mL	LCE VX_ULL.dam	A
EA2192	0.05 – 10 ng/mL	LCE VX_ULL.dam	A
VX	10 – 750 ng/mL	LCE VX_LL.dam	B
EA2192	10 – 750 ng/mL	LCE VX_LL.dam	B
EMPA	5.0 – 500 ng/mL	LCE EMPA.dam	C
VX	500 – 2000 ng/mL	GCE VX_DEANS.M	E
HD	2 – 25 ng/mL	GCE HD_DEANS.M LL	H
HD	25 – 2000 ng/mL	GCE HD_DEANS.M HL	H
H-Sulfone	10 – 2000 ng/mL	GCE H-Sulfone_DEANS.M	N
TDG	25,000 – 100,000 ng/mL	GCE TDG_DEANS.M	L
H-Sulfoxide	10 – 500 ng/mL	LCE H-Sulfoxide.dam	M
GD	2.5 – 50 ng/mL	GCE GD_DEANS.M ULL	K
GD	50 – 2000 ng/mL	GCE GD_DEANS.M LL	K
GD-acid	5,000 – 500,000 ng/mL	GCE GD-ACID_DEANS.M	O

Method listing for vapor sorbent tube samples.

Compound	Range	Method Name	Appendix Method
VX as its G analog	3 – 500 ng	GCV VX-DEANS.M	E
HD	0.1 – 500 ng	GCV HDLL-DEANS.M	F
HD	100 – 2000 ng	GCV HDHD-DEANS.M	G
GD	0.5 – 10 ng	GCV GDLL-DEANS.M	H
GD	10 – 500 ng	GCV GDHL-DEANS.M	I

REFERENCED DOCUMENTS

- DTIC published technical report by T. Lalain, et. al., titled "Development of the 2007 Chemical Decontaminant Source Document," and references therein.

- DTIC published technical report by T. Lalain, et. al., titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations," and references therein.
- Kiser, M. M.; Dolan, J. W., Selecting the Best Curve Fit. LC GC *Europe* 2004, 17, (3), 138-143.
- ARMY *Environmental Quality: Guidance for Evaluating Performance-Based Chemical Data*; EM 200-1-10; US ARMY Corps of Engineers: 2005.
- FDA Guidance for Industry: Bioanalytical Method Validation. http://www.fda.gov/cder/guidance/index.htm (December, 2007).

GUIDANCE

The methods and this guidance section are written for an audience skilled in chromatographic analysis. This section provides guidance based on the low-level development learnings that could affect the accuracy and data quality for decontaminant performance evaluations.

Calibration Curve Fitting: One of the many important factors in quantitative analysis is the accuracy of a calibration curve. The accuracy of the reported result is dependent on the accuracy of all procedures used in the preparation of a calibration curve from making the standards to the regression of the detector response to generate a 'calibration curve.' Verification that an accurate calibration curve has been acquired requires a statistical analysis of the results. A single universal indicator/value for detecting the 'right' curve or a good calibration has been an elusive goal; the evaluation of a calibration model requires several types of analysis to confirm an acceptable calibration. While the evaluation of a correlation coefficient (r) or coefficient of determination (r^2) is a common method to evaluate a calibration curve, it is not a full description of the system. The coefficient of determination (r^2) indicates a correlation between the data and the calibration; it does not indicate accuracy or lack of fit. To demonstrate how r^2 can be misleading and provide guidance on how to evaluate a calibration model, a demonstration using VX on a LC/MS/MS system is illustrated. The following demonstration illustrates the impact of weighting; the same principles apply to the selection of the calibration model (i.e., which equation to use for the calibration curve).

Figure 7F-1 shows the data collected from a LC/MS/MS for a set of VX standards. Using Matlab, a linear regression was applied to the data and calibration coefficients were determined. The r^2 value for this fit was 0.9993, indicating excellent correlation. There are several misleading aspects to Figure 7F-1. It is tempting (and often assumed) that the very high r^2 value implies a good fit and that the calibration curve is acceptable for use. Visual inspection of the curve indicates that the line goes through all of the data points, also implying a good fit. However, the dynamic range of the detector response and concentration each cover three orders of magnitude. As a result of the large dynamic range and the use of a linear graph scale the lowest four standards represent 40% of the data and are graphed on only 0.01% of the graph area. As a result, the low concentration standards cannot be visually resolved for inspection.

VX Conc. (ng/mL)	Detector Response (counts)
0.101	6,320
0.203	11,900
0.496	26,800
0.993	52,300
2.480	125,000
5.060	254,000
10.125	549,000
25.313	1,250,000
49.630	2,600,000
99.267	4,920,000

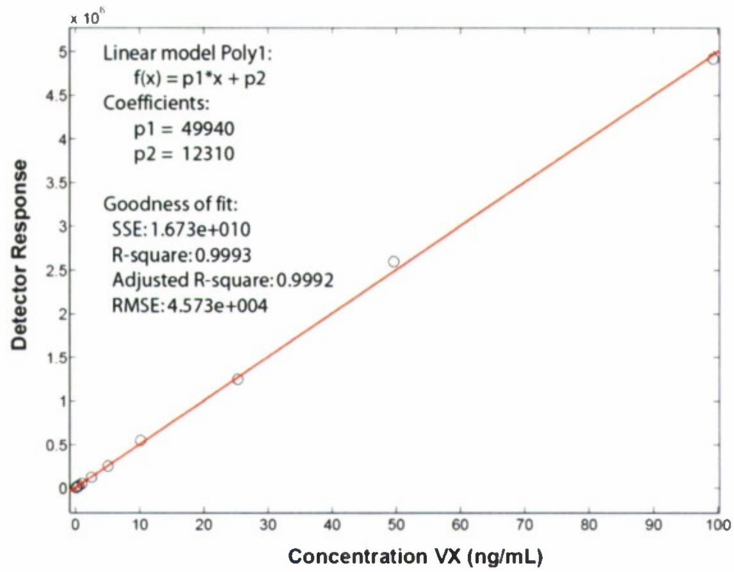

Figure 7F-1. VX calibration curve with linear plot.

To compensate for the compression of the x- and y-axes when using a linear scale, the same data should be plotted on a log-log scale, as seen in Figure 7F-2. From this graph it is immediately apparent that the calibration model does not pass through the low concentration standards. The deviation of the calibration model from the standards would impart a substantial bias to the results. Keep in mind the r^2 value for this fit was 0.9993, even with a poor fit at low concentrations. The compression of the linear scale graph did not enable this deviation to be readily observed.

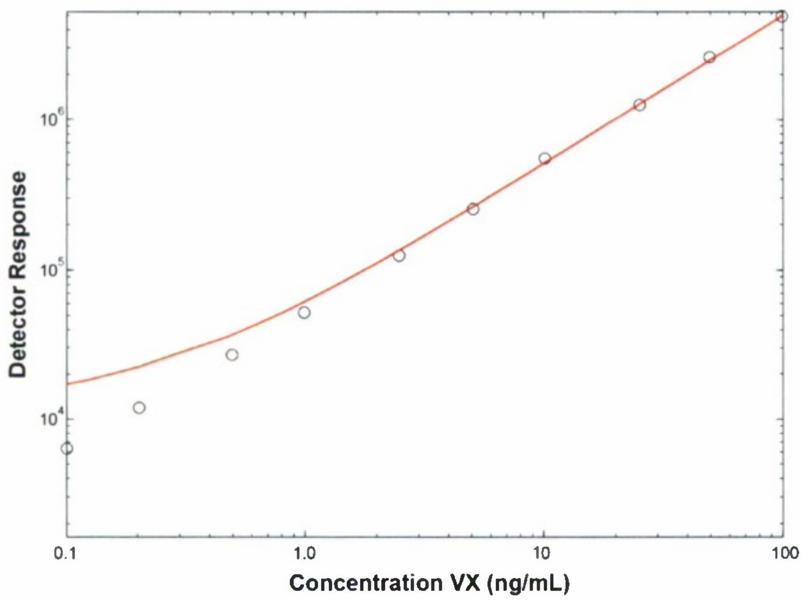

Figure 7F-2. Log-log scale VX calibration model.

This leads to the question of how much error is present in the calibration. There are several methods that can be applied to assess the error in the calibration model including residual analysis which is presented in the goodness of fit parameters in Figure 7F-1 as the sum of the square of the errors (SSE) and root mean square error (RMSE). The SSE and RMSE values

are calculated from the difference in the detector response to the calibration model response (y value) at the tested concentrations. For both SSE and RMSE a smaller value represents a better fit, however these values are not normalized and a good fit for one instrument could produce SSE values orders of magnitude different than another instrument. RMSE and SSE are excellent indicators for comparison of different models for the same data, where the smaller value indicates the better fit.

Another method to analyze error in the calibration model is to calculate the concentration (x) of a standard based on its detector response (y) from the calibration model and compare it to the known concentration. For example, applying the calibration model to the response (549,000) of the 10.125 ng/mL results in a concentration of

$$x = \frac{y-b}{m} = \frac{549000-12310}{49940} = 10.747 \text{ ng/mL} .$$

The error of the calibration model to the known concentration (C_{known}) can be calculated using two methods, relative percent deviation RPD and recovery. The RPD can be calculated as

$$RPD = \frac{C_{\text{model}} - C_{\text{known}}}{\left(\frac{C_{\text{model}} + C_{\text{known}}}{2}\right)} \times 100\% = \frac{10.747-10.125}{\left(\frac{10.747+10.125}{2}\right)} \times 100\% = 5.96\% .$$

A RPD closer to zero represents a better fit. Because this form of RPD does not use an absolute value in the numerator, the value indicates a negative or positive bias to the value. The above value indicates a slight (5.96%) positive bias (i.e., the model returns a higher concentration than the 'known' value). The second method uses the concept of recovery as defined by (FDA 2007)

$$\text{recovery} = \frac{C_{\text{model}}}{C_{\text{Known}}} \times 100\% = \frac{10.747}{10.125} \times 100\% = 106.1\% .$$

A recovery closer to 100% indicates a better fit. Similar to the RPD, the recovery value of 106.2% indicates that the model introduces a slight positive bias to the data. Both the recovery and RPD methods supply a normalized result where common acceptance criteria can be established. Standard good analytical practices use CCVs to ensure that instrument calibration is maintained throughout the run sequence; pass/fail criteria for the CCVs on a mass spectrometer is usually ±30% RPD. Because RPD is already being calculated for the CCVs, it is recommended here that RPD be used to characterize the error in the calibration model. It is recommended that the acceptance criteria for a calibration curve should be equal to or more stringent than the criteria for CCVs. Other agencies, such as the FDA, have recommended that all standards above the LOQ should have a RPD less than ±15%, and that standards at the LOQ should have an RPD less than ±20% RPD.(FDA 2007)

To continue the example of the VX calibration curve, Table 7F-2 illustrates the concentration calculated from the calibration model and the RPD for each standard. The RPD values for the lower concentrations clearly indicate a poor fit, in addition to the calibration model returning negative values at lower concentrations. If this calibration model had been accepted for use based on the r^2 value alone, low concentration samples could have underestimated the real hazard by a factor of 2 or more (assuming negative values were rejected). Ideally, if the appropriate calibration model was selected the RPD values should be equally (and randomly)

distributed about zero. A trend or curvature in a plot of concentration vs. RPD indicates that a different calibration model or weighting should be used.

Table 7F-2. RPD values for a linear regression with VX standards on LCE.

VX Concentration (ng/mL)	Detector Response (counts)	Calc. Conc. (ng/mL)	RPD (%)
0.101	6320	-0.120	-2332.61%
0.203	11900	-0.008	-216.86%
0.496	26800	0.290	-52.37%
0.993	52300	0.801	-21.43%
2.480	125000	2.257	-9.44%
5.060	254000	4.840	-4.45%
10.125	549000	10.747	5.96%
25.313	1250000	24.784	-2.11%
49.630	2600000	51.816	4.31%
99.267	4920000	98.272	-1.01%

The RPD analysis has indicated that a direct linear regression on the data does not produce an acceptable calibration model, the next question leads to how to identify the appropriate calibration model. In this case, the reason for the poor fit in the direct linear regression is related to the heteroscedasticity of the data. (Kiser 2004) Heteroscedastic data are characterized by a system where the absolute error (e.g., standard deviation) of a response varies with the abscissa (e.g., concentration). For heteroscedastic data, the standard deviation of the detector response for multiple analyses of a low level standard is smaller than that for a high level standard. However, the relative standard deviations (RSD), the standard deviation divided by the mean, for heteroscedastic data are typically consistent across concentrations. This is typical for most chromatographic detectors. If the data are homoscedastic, the standard deviations of the responses are independent of concentration.

Weighting of a calibration curve is appropriate if the data are heteroscedastic. Weighting is needed because the higher concentration standards are dominating the regression analysis. By applying a weighting to lower concentration standards, such as a 1/concentration weighting, the contributions of the low concentration standards can be balanced with the higher concentration standards. Table 7F-3 shows the impact of weighting on the calculated concentration and RPD for four weightings. The $1/x^n$ notation corresponds to $1/\text{concentration}^n$ for this data, n=0 corresponds to no weighting, n=0.5 corresponds to 1/square root(x). An additional term is introduced in the goodness of fit parameters, which is the sum of the absolute value of the RPD for all standards. Much like SSE, this value is not normalized, and a smaller number indicates a better fit. The sum of the absolute value of the RPD is a gauge for the performance of the fit across all data points. It is not optimal to select a calibration model based on the RPD for a particular standard, but rather the model that best represents all standards. For example, if the weighting was selected by only the lowest level standard (0.1 ng/mL) the $1/x^2$ weighting provides the lower RPD, however for the 0.2 ng/mL standard the 1/x weighting provides smaller RPD. It is better to look at the RPD of the system which is best represented by the sum of the absolute value of the RPDs. Note that the r^2 value changes by only 0.04% (and that the more accurate fits have the lower r^2 values) from the $1/x^2$ weighting to $1/x^0$ weighting, yet the accuracy of the calibration model is significantly different (Figure 7F-2).

Table 7F-3. Regression of the VX calibration using a linear calibration model with different weighting.

VX Known Conc. (ng/mL)	Detector Response (counts)	$1/x^0$ (none) Calc. Conc. (ng/mL) / [RPD %]	$1/x^{0.5}$ Calc. Conc. (ng/mL) / [RPD %]	$1/x^1$ Calc. Conc. (ng/mL) / [RPD %]	$1/x^2$ Calc. Conc. (ng/mL) / [RPD %]
0.101	6320	-0.120 / [2332]	0.065 / [-43.70]	0.094 / [-6.95]	0.099 / [-1.54]
0.203	11900	-0.008 / [-217]	0.176 / [-14.35]	0.205 / [0.84]	0.209 / [2.74]
0.496	26800	0.290 / [-52.37]	0.472 / [-4.89]	0.500 / [0.76]	0.500 / [0.85]
0.993	52300	0.801 / [-21.43]	0.980 / [-1.34]	1.005 / [1.17]	0.999 / [0.63]
2.480	125000	2.26 / [-9.44]	2.43 / [-2.18]	2.44 / [-1.45]	2.42 / [-2.37]
5.060	254000	4.84 / [-4.45]	4.99 / [-1.32]	5.00 / [-1.22]	4.95 / [-2.27]
10.125	549000	10.75 / [5.96]	10.86 / [7.05]	10.84 / [6.82]	10.72 / [5.70]
25.313	1250000	24.78 / [-2.11]	24.82 / [-1.99]	24.72 / [-2.36]	24.44 / [-3.52]
49.630	2600000	51.82 / [4.31]	51.68 / [4.05]	51.45 / [3.61]	50.86 / [2.44]
99.267	4920000	98.3 / [-1.01]	97.85 / [-1.44]	97.40 / [-1.90]	96.26 / [-3.08]
Regression	Slope $\left(\frac{counts}{ng/mL}\right)$	49940	50250	50500	51100
	Intercept (counts)	12310	3065	1562	1238
	Weight	$1/x^0$ (none)	$1/x^{0.5}$	$1/x^1$	$1/x^2$
Goodness of Fit	r^2 (unitless)	0.99928	0.99927	0.9991	0.9989
	SSE (counts)	1.67E+10	2.60E+09	4.30E+08	2.18E+07
	RMSE (counts)	45727	18031	7331	1650
	$\sum\lvert RPD\rvert$ (%)	2650	82.29	27.09	25.15

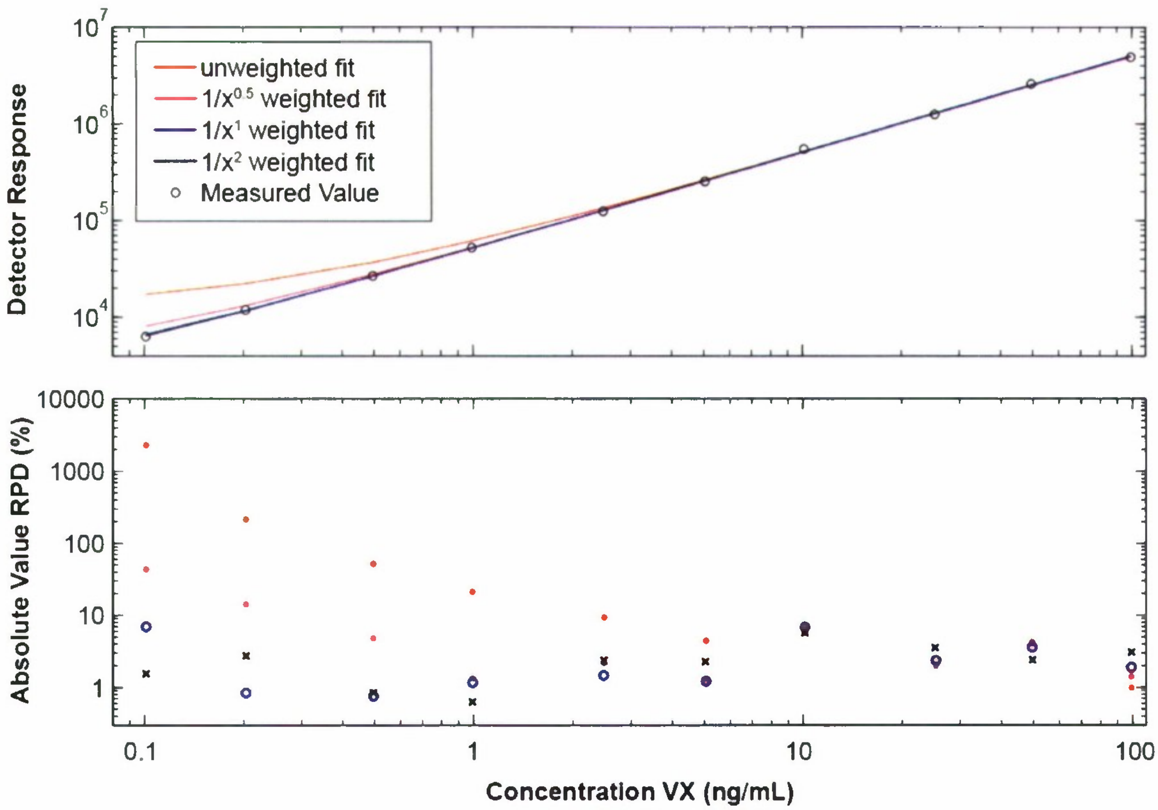

Figure 7F-3. Calibration and RPD graphs for VX with weighting.

Based on the results in Table 7F-2 and Figure 7F-2, the 1/x and $1/x^2$ weighted regressions provide the best fit. The next question is which is better to use. At this point, it is recommended to choose the weighting that provides the smallest sum of absolute value of RPDs (Kiser 2004), in this case the $1/x^2$ weighting. There are statistical tests that can be used to evaluate calibration curves such as the F-test (or a Mandel Fitting Test); however, caution should be used with applying these tests as equal weighting is assumed for all data points and will likely indicate the unweighted model as the better fit.

Overall, it is suggested that the calibration be reported by providing the known concentrations, the detector responses and the RPD for each standard in addition to the calibration model, weighting, r^2, and coefficients. Acceptance of a calibration curve based on r^2 alone does not imply accuracy, the RPD for every standard should meet an acceptance criteria (e.g., RPD < 15%). Providing all of this information demonstrates the accuracy of the calibration and enables reprocessing of the data if it is determined that an inappropriate calibration model was selected.

Quality Control Samples and Sample Queues: Even with the acquisition of an acceptable calibration curve, there is the possibility that the instrument calibration could drift or change during the analysis of samples. The best way to prevent these issues is to keep the instrument well maintained, however even the best maintained instrument may drift during an analysis. To ensure confidence that accurate results are generated, quality control samples should be analyzed during a run. The order that the standards, analytical samples, and QC samples are run in is referred to as the sample sequence or sample queue (used interchangeably). Most often, the instrument control software calls this order a sequence. Logic should be applied in the organization of the sample queue as effects such as carryover, interferents, or instrument

drift could invalidate large sets of data. The following guidance discusses what each type of QC sample is, what it indicates, how it is used, and finally how the QC samples should be integrated into the sample queue.

Quality control samples are used to ensure confidence in the reported analytical value. QC samples enable trend analysis, determination of bias in sample analysis, detection of instrument drift, carryover, and provide information on the error in the reported analytical value. QC samples include initial concentrate verification (ICVs), continuing concentration verification (CCVs) and blank samples. If the QC samples do not meet performance criteria, it is an indication of a possible problem that must be corrected to ensure confidence in the analytical data.

ICVs are used to verify that a standard of known concentration is accurately determined by the instrument and calibration model. Although not required, an ICV should be a standard that was **not** used to generate the calibration curve. The accuracy of the ICV sample can be calculated using a relative percent deviation (RPD) as defined by

$$RPD_{ICV} = \frac{C_{\text{Calc}} - C_{\text{known}}}{\left(\frac{C_{\text{Calc}} + C_{\text{known}}}{2}\right)} \times 100\%,$$

where

C_{Calc} = concentration/mass calculated from the calibration model,
C_{known} = known concentration/mass of sample.

Acceptance criteria for the ICV should be established, typical values would be in the range of ±15-30% RPD. An ICV with an RPD within the acceptance criteria indicates a successful calibration; failure to meet the ICV acceptance criteria indicates low confidence in the calibration curve and thus low confidence in the data produced from the calibration. ICV samples are typically run shortly after the standards in the queue, discussed later in this document.

The sensitivity of an analytical instrument can change over time for various reasons including: build-up of analyte, presence of interferents from samples, variations in room temperature, or the need to perform maintenance such as changing an injection port septum, conditioning, or replacement of the column. To confirm that the performance of the system does not change (i.e., the calibration changed or drifted) during a sequence, use of continuing calibration verification (CCV) samples is required. A CCV sample is often a rerun of a standard as a confirmation that the measured concentration has not changed, and thus the instrument is performing consistently. This can be accomplished by calculating the RPD of the calculated concentration of the CCV sample (C_{Calc}) to the known concentration (C_{known}) as given by

$$RPD_{CCV} = \frac{C_{Calc} - C_{known}}{\left(\frac{C_{Calc} + C_{known}}{2}\right)} \times 100\%.$$

Acceptance criteria are established to determine if a CCV indicates an acceptance or failure to hold calibration. Typically a value of greater than ±30% RPD is used as failure criteria for a MSD. The variation in concentration/mass of CCV samples is a result of errors from both systematic and random sources. The 30% performance criterion is a commonly accepted standard. If a failure is detected, corrective actions must be taken to return the instrument to

calibration (e.g., instrument maintenance, rerun standards, etc.). Further samples acquired before and after a failed CCV are suspect and will need to be rerun, as discussed later.

It is recommended that more than one concentration be tested as a CCV, selection of which concentrations to use is dependent on the objective of the experiment. Overall, the CCV concentration should correspond to the concentrations expected from the test. It is expected that most decontamination tests will be attempting to meet a requirement, thus it would be advisable to include a CCV near the requirement concentration and one at a mid to high end of calibration. Other government organizations such as the FDA recommend three values corresponding to ~3 times the LOQ, midrange and high range concentrations for CCVs. (FDA 2007) The quality sample and acceptance methods used by a laboratory should be documented in the final report as there are several guides and methods that can be utilized.

The last type of QC sample discussed here is the use of blanks. A blank sample is a sample containing only the extract solvent (or uncontaminated vapor tube). A blank should not elicit a detector response at the expected retention time of the analyte of interest. Blanks are an effective means of evaluating baseline performance and confirming there is no analyte carry-over in the system. Analyte carry-over is the detection of an analyte in one sample that was the result of the analysis of a previous sample. The result of analyte carry-over is a positive bias in a sample, present mostly in low concentration/mass samples. When running a solvent blank, a detector response noted at the expected retention time can be indicative of carry-over of high concentration/mass samples, interferences, a dirty system or other problem that may affect the identification and quantitation of the analyte of interest. Blank samples are included in the sample queue at regular intervals to check for carry-over, as discussed later. The acceptance criteria for the blank or solvent only sample is that the reported concentration must be below the LOD for the analysis method. This criterion was established to ensure that any carryover would not appreciably affect the results of the sample analyzed next in the sequence.

The acquisition of a successful calibration model indicates an instrument that is calibrated under ideal conditions. As samples are analyzed over a period of time (runs can last from 1-36+ hours and include 1-100+ samples), many things could happen to the analytical system that could change the instrument sensitivity and performance, as previously discussed. For this reason QC samples must occur at regular intervals during the sample queue to confirm the analytical instrument is performing within specifications.

In addition to the QC samples, consideration should be applied to the order that the samples are run. In decontamination testing some samples may have concentrations that are significantly different (e.g., the contact-test for a bare metal vs. an elastomer). If there is any carry-over in a system, a very high concentration sample followed by a low concentration sample could yield a false high (i.e., positive bias) concentration in the low concentration sample. For this reason it is advisable for the operator to use best judgment in the organization of samples to prevent this situation. In addition to the sample concentration, some samples are 'cleaner' than others. For example, the contact test involves the extraction of a contact sampler that has been acetone rinsed to remove impurities. This extraction is relatively clean in that the only compounds in the extract solution are likely the agent and possibly some agent reaction byproducts. In comparison, residual agent extractions are in some cases not 'clean' in that the extraction process may have removed other compounds from the coupon (e.g., plasticizers extracted from elastomers like silicone). It is possible that some interferents extracted from the coupons may alter the performance of the analytical instrumentation (e.g., interferents coating the column), this could be detected by failing CCVs or positive blanks. To minimize rerunning large numbers of samples it is advisable to put samples that are 'dirty' or likely to contain impurities together at

the end of a queue. If the interferents are significant enough, sample clean-up procedures (e.g., solid phase extraction) may be needed to accurately analyze the samples and prevent damaging the analytical instrumentation (e.g., destroying the column). In summary, it is best to run the 'cleanest' samples first and order the samples from anticipated lowest concentration to highest concentration.

In most cases a queue is initiated with a series of blanks followed by the standards, another blank, an ICV, a CCV block, then samples, with iterations of CCV blocks and samples until the queue is complete, terminating with a CCV block. Figure 7F-4 provides a demonstrative sample queue. The first blank ensures that the system is 'warmed' up and flushed out, the second blank can be used to verify the system is clean and there is no carry over from previous runs. The standards are then run from lowest to highest concentration (minimizing the effect of any potential carry-over). The blank run after the highest standard is primarily used to detect any carry-over in the system. Because this blank follows the highest concentration anticipated to be run in this sequence, if carry-over is occurring it will be reflected in this sample. The ICV sample is then run to confirm that an acceptable calibration was acquired.

After the ICV, the following sample begins a CCV block. In this example a CCV block consists of a blank, a low level CCV (1 ng/mL) and a mid level CCV (50 ng/mL). After a CCV block, a set of samples is run, followed by another CCV block. The CCVs surrounding the samples are said to 'bracket' the samples. For a set of samples to be accepted both bracketing CCV blocks must pass. In the event of a QC sample failing to meet an acceptance criteria (e.g., blank detecting carryover or CCV > 30% RPD), the samples preceding and following the CCV block are suspect and should be rerun. It is not possible to identify when the instrument was failing to meet specifications, thus all samples between the last passing QC sample and the failing sample should be rerun. In addition to this guidance, other documents such as Chapter 9 of the US Army Engineering Manual EM200-1-10 can be used to accept or reject data.

The frequency of CCV blocks is a balance of instrument run time and confidence in instrument performance. For example, given the frequency of nine samples per CCV block, the failure of one CCV block would dictate that 18 samples are rerun (the samples before and after the failing CCV block). Selecting a large number of samples between CCV blocks results in a shorter total queue run-time, however, a CCV block failure results in a significant number of samples to rerun. Conversely, running a CCV block between every sample is also not practical. Typical intervals for CCV blocks are 5-20 samples. If particular samples are expected to cause instrumentation problems, or extra confidence is desired, CCV blocks can be run more often.

Queue Number	Sample Type	Known Conc. (ng/ml)	Sample Name
1	blank	0.0	blank00
2	blank	0.0	blank01
3	std	0.1	0.1std
4	std	0.2	0.2std
5	std	0.5	0.5std
6	std	1	1std
7	std	2.5	2.5std
8	std	5	5std
9	std	10	10std
10	std	25	25std
11	std	50	50std
12	std	100	100std
13	blank	0	blank02
14	ICV	7	7ICV
15	blank	0	blank03
16	CCV	1	1CCV1
17	CCV	50	50CCV1
18	sample		sample1
19	sample		sample2
20	sample		sample3
21	sample		sample4
22	sample		sample5
23	sample		sample6
24	sample		sample7
25	sample		sample8
26	sample		sample9
27	blank	0	blank04
28	CCV	1	1CCV2
29	CCV	50	50CCV2
30	sample		sample10
⋮			⋮

Comments:

Ensure 'warm up' and 'clean' system.

Run Standards

Check for carry-over

Check ICV

Test blank and CCVs

Samples 1-9 are bracketed by CCVs 1 and 2

Test blank and CCVs

Green = QC Sample

Blue = Standards

Black = Samples

Figure 7F-4. Example analytical queue with QC samples

VAPOR SORBENT TUBE GUIDANCE

Vapor sample queues should also consider the amount of agent on the sorbent tubes. The chance for sample carrier over is greater with vapor sorbent tube analyses. The analysis of the low-mass containing tubes first in a sample queue is encouraged to minimize positive bias should a higher-mass tube result in carryover. Sample tubes expected to contain higher mass should be analyzed later in the sample queue if possible. If there is concern that selected samples may result in carry over, then blank tubes can be placed between those samples to determine if carryover occurred. The art of vapor sample analysis comes with experience. In most cases, a scoping test with a few samples can provide this information prior to performance of a full test with multiple replicates.

The use of solid sorbent tube requires a few additional considerations to ensure optimum performance. The tubes should be used and analyzed in accordance with manufacturer instructions. Some considerations for successful decontaminant performance evaluations are provided in this section.

- **New tube receipt**: most manufacturers recommend an initial conditioning process to remove any contaminants from the sorbent materials as a result of the manufacturing or shipment process prior to first use.
- **Tube spiking**: tube spiking is the process of making analytical calibration samples for vapor analysis and is accomplished by introducing a specified volume of liquid chemical agent standard prepared in high purity solvent to the sorbent material contained within the tube. Tube spiking should be performed on conditioned and verified-clean tubes. Tube spiking is the introduction of a known volume of a particular concentration of liquid chemical agent standard with a microliter (µL) syringe onto the sorbent material of a tube. The tube must have air flow to pull the standard onto the sorbent bed and to aspirate away the solvent in which the standard was delivered. Tube spiking and sample collection are always done on the same end of the tube. Sample analysis must desorb the sample from the same end that the sample was collected or spiked upon.
- **Tube conditioning**: Per the manufacturer, solid sorbent tubes are typically reusable for about 100 heating cycles. Because they are reused, one challenge is to ensure that reused tubes are 'clean' before being placed back into circulation. If the sorbent material has retained any agent from the previous sampling/desorption cycle, it will induce a positive bias in the results of the next sample. The retention of analyte on a tube after analysis is called carry-over. To prevent carry-over from interfering with the next sample/analysis cycle, the tubes are conditioned, or cleaned. To verify that the tubes have been cleaned a representative sampling of the total number of conditioned tubes are re-analyzed and verified blank. There is commercial hardware available to condition and clean tubes between uses. Tube conditioners typically heat the tubes to a specified temperature (usually above the desorption temperature for most analytes but below the breakdown temperature of the sorbent) and nitrogen or air is purged through the tube to desorb any residual analytes.
- **Chromatographic confirmation of conditioning**: In order to ensure that the sorbent tubes are "clean enough" to be used to generate instrument calibration curves or to be used for sample collection, they must be checked after cleaning. Checking each sorbent tube individually would be labor intensive. The American National Standard Z 1.4 "Sampling Procedures and Tables for Inspection By Attributes" provides sampling plans that can provide a high level of confidence that batches of sorbent tubes are clean and ready for use without requiring the analysis of each individual tube. The sampling plans in the standard were designed such that the more "defects or items failing the acceptance criteria" a batch or lot contains the more likely that it will be rejected. In this case, if a batch of sorbent tubes fails to meet the acceptance criteria, the batch of sorbent tubes would undergo a second cleaning.

REPORTING

The following information must be documented in the test report for this procedure. Most of the required reporting information can be captured in the experimental section.

The experimental section should include a description of the analytical equipment used including configuration and software operating platform. The report should contain a description of the analytical methods used including the calibration range, calibration standard preparation, calibration model, calibration weighting, limit of detection, limit of quantitation, quant ions used, column. The report should also include a description of the quality control and assurance procedures such as use of initial and continuous calibration samples (ICV, CCV) and solvent blanks; non-detect, below-detect and below quantiation result reporting criteria; sample dilution procedures; and data acceptance criteria. For most reports, this information may be best captured in the experimental and referred to in the test result and discussion sections.

Test data collected outside the calibrated range should be documented as such. A non-detect (ND) should only be reported when a true non-detect is observed. Sample analysis identifying agent present below the method calibration limit or quantitation limit should be reported as below detection (BD) or below quantitation (BQ) as appropriate. An estimated quant value can be provided, but should be documented indicating that the value is an estimate and below method detection or quantitation. The analysis of extract samples resulting in values above the calibration range can typically be diluted to enable analysis within the analytical method range. Results should be clearly noted so that unfamiliar readers do not incorrectly assume that a result is suspect because it is greater than the analytical method calibration range.

REVISION HISTORY

March 2008: Original method.

Section 8: Detection and Protection Test Methods

DESCRIPTION

This section contains the detection and protection test procedures documented in TOP 8-2-061 (Initial Release) dated November 19, 2002 that were not updated as part of the FY06-07 test program. The methods were reviewed during this effort and recommended reporting additions provided.

CONTENTS

8A - Convective Flow for Air Permeable Materials Test Method*

8B - Detector Compatibility Test with Decontaminant*

8C - Individual Protective Equipment and Collective Protective Equipment Compatibility*

NOTES

*Method not updated as part of FY06-FY07 effort.

Test Procedure 8-A: Convective Flow for Air Permeable Materials Test Method

SUMMARY OF PROCEDURE

According to the 2002 TOP 8-2-061, "the objective of this live-agent test is to measure the ability of an air-permeable material to resist convective penetration of a chemical agent after the material had been contaminated with a decontamination solution."

TERMINOLOGY

No specific terms defined for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002.

REFERENCED DOCUMENTS

U.S. Army Test and Evaluation Command (TECOM), Aberdeen Proving Ground, Maryland, Test Operations Procedure (TOP) 8-2-501, Permeation and Penetration Testing of Air-Permeable, Semi-Permeable Materials with Chemical Agents or Simulants (Swatch Testing), 3 March 1997.

REAGENTS, MATERIALS AND EQUIPMENT

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

Procedure

a. The objective of this live-agent test is to measure the ability of an air-permeable material to resist convective penetration of a chemical agent after the material had been contaminated with a decontamination solution. This test will be performed IAW Reference 14.

b. The decontamination solution will be checked before the test for interference (GC peak) and reaction of the decontamination solution vapor with agent.

c. The testing conditions will be 80 ± 3 % RH and 32.2 ± 1.1 °C (90 ± 2 °F).

d. A 10 cm^2 sample swatch of the material will be contaminated with 2 mL of the decontamination solution and exposed to the decontaminant for 1 hr.

e. The sample swatch will be dried under test conditions for 30 min and then tested using a liquid challenge/vapor penetration (L/V) convective penetration method.

f. The sample will be contaminated with 10 g/m^2 (10 x 1 µL drops on 10 cm^2 sample swatch) of agent, and then an air-flow (at a pressure of 0.1 inches of water) will be introduced through the material.

g. Any chemical agent vapor breaking through the two layers of the material will be measured (via bubbler) over a 24 hr period.

h. Bubbler samples will be taken after 6-, 16- and 24 hr, or as specified by the test sponsor.

i. Convective flow results: average weight of agent penetration per unit area of material measured over 24 hr

TEST REPORTING

Documentation should include the following information:

- the actual test temperature and relative humidity conditions
- the device used to measure the temperature and humidity
- the type of decontaminant solution used, including concentration and date of preparation
- the time test started and each bubbler sampling times
- the times of bubbler samples if different than TOP procedure and justification for the additional sampling
- list all equipment by model and calibration status
- any other requirements per referenced TOP 8-2-510.

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

REVISION HISTORY

Mar. 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method are shown in underlined, italicized text.

Test Procedure 8-B: Detector Compatibility Test With Decontaminant

SUMMARY OF PROCEDURE

According to the 2002 TOP 8-2-061, "this test procedure is for the determination of the impact a decontaminant has on the ability of a detector to perform in the presence of decontaminant."

TERMINOLOGY

No specific terms defined for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002.

REFERENCED DOCUMENTS

No specific references cited for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002.

REAGENTS, MATERIALS AND EQUIPMENT

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE AND REPORTING

General

(1) All detectors will be checked for correct functioning before any other testing. Record results of function checks. <u>*The initial functionality testing documentation for each detector should include:*</u>

  a. <u>*Detector type: including common name, model, serial number*</u>
  b. <u>*Date of test*</u>
  c. <u>*Agent or simulant used for test*</u>
  d. <u>*Brief description of the functionality test including number of trials*</u>
  e. <u>*Functionality test results*</u>
  f. <u>*Documentation of any damage to the detector unit (photographs recommended to note any damage that might impact performance)*</u>

(2) Number of replicates conducted shall be sufficient to demonstrate high, statistical confidence in results or as specifically identified by the test sponsor. <u>*No less than 5 replicates for a given test are recommended.*</u>

(3) Detectors/alarms used shall be as specified by the test sponsor, but are expected to include the following:

  a. Improved Chemical Agent Monitor (ICAM).
  b. U.S. Marine Corp (USMC) Chemical Agent Monitor (CAM).
  c. M43A1.
  d. M90D1-C.

e. M18A2.
f. M256A1.
g. Shipboard Chemical Agent Monitor – Portable (SCAMP).
h. Improved Point Detection System (IPDS).
i. AP2C.
j. Lightweight Chemical Detector (LCD).
k. Joint Chemical Agent Detector (JCAD).
l. M8 and M9 detector paper and tape.
m. M272 Water Testing Kit
n. Chemical Biological Mass Spectrometer (CBMS).
o. Biological Aerosol Warning Sensor (BAWS).
p. Hand-Held Assay (HHA).
q. Automatic Chemical Agent Detector and Alarm (ACADA).

(4) Agent to decontaminant ratio: Optimize decontaminant to agent ratio and verify prior to test.

False Positive vs. Neat Decontaminant

(1) A false positive is defined as the detector alarming to the presence of the neat decontaminant with no agent present.
(2) Decontaminant will be prepared according to IAW manufacturers or test sponsor's instruction will be placed in a glass dish in a fume hood (face velocity 100 to 150 ft/min which equates to 1 to 2 mph wind speed).
(3) The inlet of the detector (itself or attached with a flexible Teflon® tube) will be placed approximately 2.5 cm (1 in) above the specimen surface to collect the sample vapor.
(4) The detector will be allowed to sample until the unit alarms or until the detector sample time is reached, or up to 5 min if there is no sample time specified. Precautions will be taken to prevent gross contamination of the detectors. Spectra or recordings will be taken when appropriate.
(5) All detectors responses, aforementioned data requirements, and any conditions or observations deemed potentially relevant to the experiments will also be noted in laboratory notebooks and discussed in the data report.
(6) The appropriate function check will be conducted before and after the test is complete.

False Negative vs. Agent-Decontaminant Mixture

(1) A false negative is defined as the decontaminant masking the agent (not reacted) in such a way that the detector does not alarm to indicate agent present.
(2) Before testing begins, the functionality of the detectors will be verified.
(3) The decontaminant will be placed in a beaker.
(4) A syringe will measure the required amount of agent and transfer it onto the decontaminant in the beaker. The test will be performed with 10 mg each of VX, HD, and GD. Each agent will be tested separately.
(5) The decontaminant will be mixed thoroughly with the agent.
(6) The beaker will be covered with one-half of a Petri dish.
(7) The agent-decontaminant mixture will weather for 10 min.
(8) The Petri dish will be removed during sampling and replaced after each sample period.
(9) Each detector will be placed to sample the air in the headspace of the beaker.
(10) The detectors will sample the air based on the manufacturers recommended time and at the time intervals specified by the test sponsor.

(11) The operator will observe for a response (or lack of response) and response time, while a second individual will annotate the observations. The detectors will be allowed to clear from the exposure (clear down) before simulant checks or new agent exposures are conducted.

(12) The functionality of the detectors will again be verified

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

REVISION HISTORY

Mar. 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates are required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional recording and reporting requirements added to the test method and are shown in underlined, italicized text.

Test Procedure 8-C: Individual Protective Equipment and Collective Protective Equipment Compatibility

SUMMARY OF PROCEDURE

According to the 2002 TOP 8-2-061, "this test determines the effects of decontaminant exposure on individual and collective protection systems hardware. This test is designed to measure any degradation caused by the decontaminant on selective aspects of the system's performance from that of the baseline performance established in the Individual Protective Equipment (IPE) and Collective Protective Equipment (CPE) product performance specifications."

TERMINOLOGY

No specific terms defined for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002.

REFERENCED DOCUMENTS

U.S. Army Test and Evaluation Command (TECOM), Aberdeen Proving Ground, Maryland, Test Operations Procedure (TOP) 8-2-501, Permeation and Penetration Testing of Air-Permeable, Semi-Permeable Materials with Chemical Agents or Simulants (Swatch Testing), 3 March 1997.

REAGENTS, MATERIALS AND EQUIPMENT

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

SAFETY PRECAUTIONS

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

PROCEDURE

General

(1) This test determines the effects of decontaminant exposure on individual and collective protection systems hardware. This test is designed to measure any degradation caused by the decontaminant on selective aspects of the system's performance from that of the baseline performance established in the Individual Protective Equipment (IPE) and Collective Protective Equipment (CPE) product performance specifications.

(2) The test may be required to be conducted at low [~-32 °C (~-25°F)], ambient [21 °C (~70 °F)], and high [~49 °C (~120 °F)] temperatures, and at low (< 20%) and high (> 90%) RH.

Procedure

(1) Using test fixtures and facilities specified by the test sponsor, the test item will be configured for exposure challenge with the test decontaminant.

(2) Decontaminant will be applied to the test item in the amount, manner, and duration specified by the test sponsor.
(3) The test item will be evaluated periodically (as specified by the test sponsor) during the conduct of the test and on the completion of the test for compliance with the sponsor's selected requirements from the product's performance specifications. Additional test item performance requirements may be evaluated as specified by the test sponsor. Selected test items may be set aside for evaluation of long term exposure effects.
(4) Testing of the physical properties of the test item's materials of manufacture may be performed during the course of the testing and/or on completion of testing at the request of the test sponsor.

TEST REPORTING

The following data will be reported:

(a) Test conditions: *to include specific temperature and relative humidity*.
(b) Type (*supplier, description, lot or other batch identifying information, expiration date when applicable)*, quantity, and concentration of decontaminant applied.
(c) Mode and location of decontaminant application.
(d) Duration of decontaminant application: *to include how applied and for how long*.
(e) Observed test item physical effects, such as changes in consistency and color.
(f) Product performance data as required by the performance specification, or as requested by the test sponsor.
(g) Physical properties of test item materials.
(h) *All deviations from the test procedure will be documented and reason for deviation provided.*
(i) *Any other references used during testing*
(j) *Any other documentation requirements from TOP 8-2-501.*

DATA ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

CALCULATIONS

No specific list for this test in TOP 8-2-061 (Initial Release) dated November 19, 2002 in the test section; however, may be embedded in the front matter list.

REVISION HISTORY

Mar. 2008: This test procedure was not updated as part of the FY06-07 test program; however, the methods were documented in this Source Document for completeness. No new analytical data was generated in order to evaluate the test procedure performance to determine if updates were required. The only modifications to this test method were to provide additional guidance for the test documentation to ensure pertinent information is recorded during testing. The additional reporting requirements added to the test method are shown in underlined, italicized text.

Sub-Appendix A: Acronym List and Glossary

ACRYONYM AND ABBREVIATION LIST

The acronyms and abbreviations used throughout this document for chemical decontaminant testing protocols are listed in this Appendix. The acronyms and abbreviations are divided based on general category. Laboratories using these methods should avoid using acronyms that overlap with document specific acronyms. All laboratory specific acronyms used in test documentation not listed in this Appendix should be defined in the test plan and report on first usage.

Group 1: Basic Laboratory Abbreviations and Measurements

hr	hour
hrs	hours
mL	milliliter
ng	nanogram
µL	microliter

Group 2: General Test Method

ACN	analytical control number
AR	Army Regulation
ATP	abbreviated test plan
CAR	corrective action report
CARC	Chemical Agent Resistant Coating
CoC	chain of custody
CPE	Collective Protective Equipment
DTP	detailed test plan
EA	environmental assessment
EIALC	Environmental Impact Assessment for Life Cycle
EIS	Environmental Impact Statement
FM	Field Manual
IAW	in accordance with
IPE	Individual Protective Equipment
IPT	Integrated Product Team
KPP	key performance parameters
L/V	liquid challenge/vapor penetration
MIL-STD	military standard
MS	mass spectrometry
MSDS	material safety data sheet
NEPA	National Environmental Policy Act
ORD	Operational Requirements Document
ORI	operational readiness inspection
QA	quality assurance
QC	quality control
REC	Record of environmental consideration
RDT&E	research, development, test, and evaluation
RH	relative humidity
SAR	Safety Assessment Report
SCG	Security Classification Guide
SEP	System Evaluation Plan
SICN	sample item control number

SOP	Standing Operation Procedure
SSP	System Support Package
TCN	trial by trial control number
TD	test director
TIC	toxic industrial chemical
TICN	test item control number
TIR	test incident report
TIWG	test integration working group
TOP	Test Operations Procedure
TRR	test readiness review

Group 3: General Test Equipment

AED	atomic emission detection
DAAMS	Depot Area Air Monitoring System
FID	flame ionization detection
FPD	flame photometric detection
GC	gas chromatograph
HEPA	high-efficiency particulate air
IR	infrared
LC	liquid chromatography
MS	mass spectrometry
NMR	nuclear magnetic resonance

Group 4: Chemical Agent Specific

CASARM	Chemical Agent Standard Analytical Reference Materials
GA	tabun
GB	sarin
GD	soman, non-persistent agent
HD	distilled mustard, blister agent
TGD	thickened soman
VX	methylphosphonothioic acid, persistent nerve agent

Group 5: Chemical Agent Simulant Specific

DEM	diethyl malonate
MeS	methyl salicylate
PEG200	Polyethylene glycol 200
TEP	triethyl phosphate

Group 6: Detectors

ACADA	Automatic Chemical Agent Detector and Alarm
ACAMS	Automatic Continuous Air Monitoring System
CAM	Chemical Agent Monitor
HHA	Hand-Held Assay
ICAM	Improved Chemical Agent Monitor
IPDS	Improved Point Detection System
JCAD	Joint Chemical Agent Detector
LCD	Lightweight Chemical Detector
MINICAMS®	Miniature Automatic Continuous Air Monitoring System®
MIRAN®	Miniature Infrared Analyzer®
RTM	Real-Time Monitor
SCAMP	Shipboard Chemical Agent Monitor Portable

Group 7: Agency or Program Specific

ASTM	American Society for Testing and Materials
CB	chemical and biological
DOT	Department of Transportation
DPG	U.S. Army Dugway Proving Ground
DTC	U.S. Army Developmental Test Command
ECBC	Edgewood Chemical Biological Center
EPA	Environmental Protection Agency
JSFDS	Joint Service Family Decontamination System
JSLIST	Joint Service Lightweight Integrated Suit Technology
NBC	nuclear, biological, and chemical
RDECOM	Research and Development Command
USMC	U.S. Marine Corp

TERMINOLOGY GLOSSARY

This section contains the definitions for key terminology in this document. Some of the definitions are focused on the specific use or context of the test method. The use of these terms in reports should align with the meaning used in this document. If the term has a different meaning, the author should define the term in the final report.

- **absorption**: the uptake of a contaminant INTO the volume of a material. The contaminant must transport through the surface into the volume of the material
- **adsorption**: the adhesion of a contaminant on a material. This is limited to the surface of the material and does not include contaminant residing inside the material.
- **air change rate**: the ratio of air flow rate / vapor chamber volume (units: $hour^{-1}$).
- **agent**: see chemical agent. Used interchangeably with contaminant.
- **ambient temperature**: the temperature of the surrounding air (EPA), in this case the surrounding air is defined as the temperature in the working environment (i.e., the laboratory/hood). This is the same as room condition.
- **analytical sample**: liquid extract or vapor tube sample generated during the coupon testing for chromatographic analysis (GC and/or LC) or other quantitative analytical tools.
- **bioavailable:** in toxicology, the degree to which a substance becomes available to the target tissue after administration of a defined exposure. In regard to the contact test, the contaminant mass transferred to the contact sampler that could be biologically available under appropriate conditions.
- **breadboard, brassboard, prototype**: technology in differing degrees of configuration still under development that is not in final form. This can apply to test fixtures, formulations and/or the decontamination system / applicator.
- **calculations, approximated** : a calculation is described as approximated in cases wherenot all variables are measured but the most pertinent data is collected. Approximated values may not account for some forms of systematic loss (e.g., evaporative loss between touches in the contact test); however the desired value can be determined within the specified assumptions or limitations. It must be recognized that some degree of inaccuracy is inherent.
- **calculations, calculated** : a calculation is described as calculated in cases where the optimal test was executed and all pertinent values were measured. This type of calculation offers the highest level of confidence in the accuracy of the value.
- **calculations, inferred** : a calculation is described as inferred if gross assumptions are made regarding some variables used in the calculation. This type of calculation offers a lower confidence level in the accuracy of the value.
- **chemical agent:** is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in FM 3-11.9. The term agent is used interchangeably with the term contaminant.
- **confidence interval**: is a calculated range for a data set that future results are likely to fall between.

- **contact hazard:** the amount of contaminant remaining on the surface that, based on toxicological human estimates, could pose a threat to unprotected personnel touching the contaminated surface.
- **contact mass:** a uniform mass used to apply pressure during the contact test. The masses are typically prepared from stainless steel. The masses should evenly exert 0.7-1.0 psi pressure on the coupon surface. For the 2 in. diameter disk, this is equivalent to a 2 in. diameter cylindrical mass weighing 1 kg.
- **contact sampler:** material used in this contact test as a surrogate for human skin. The sample sorbs the available surface contamination which is then extracted to determine the mass of agent potentially bioavailable or available for contact transfer.
- **contact sampler transfer efficiency:** the measurement of the contact sampler's ability to collect the contaminant from the test material (e.g., coupon). More specifically, the contact sampler's ability to sorb the analyte under the ideal case by using a nonsorptive material. Transfer efficiency may be different for material-agent combinations.
- **contact transfer:** the capability for a contaminant present on a specific surface to be moved to another through touching the contaminated surface.
- **contaminant:** a chemical compound with harmful effects to humans to be neutralized or removed from surfaces of interest. Typical contaminants include chemical agents, chemical agent simulants, toxic industrial chemical and toxic industrial materials. A list of contaminants is provided in Appendix B.
- **contamination:** the deposition, adsorption, or absorption of chemical agents on or by structures, areas, personnel, or objects. (reference FM 3-11.9)
- **contaminant simulant:** compounds of lower toxicity that contain at least one property similar to the parent contaminant (e.g., live chemical agent).
- **contamination set:** for dose confirmation, a contamination set is a specific contamination density, drop volume, and deposition pattern combination. Deposition pattern only matters if the contaminant application uses more than 1 drop.
- **coupon:** test sample used for test methods requiring representative material surfaces. Coupons are prepared by cutting original stock material to the size needed for testing. The word panel is used interchangeably with coupon.
- **coupon surface area**: the geometric area of the surface of a coupon (for a 2 in. diameter disk = 20.2 cm^2). This area does not account for microscopic surface roughness.
- **coupon handling**: treatment of the coupons upon leaving inventory through disposal. Handling may include contamination, decontamination, extraction, etc.
- **decontaminant:** for these procedures, a substance with the capability to remove and/or neutralize chemical agents on/in surfaces of interest. The decontaminant can be liquid-phase, solid-phase (powders, wipes), or gas-phase (fumigants, including aerosols). A summary list of decontaminants is provided in Appendix B.
- **decontamination process:** The process of making any person, object, or area safe by absorbing, destroying, neutralizing, making harmless, or removing a contaminant. (reference FM 3-11.9) More specifically for these procedures, the specific series of coupon treatment tasks performed which may include contaminating, aging, decontaminating, rinsing and drying.

- **detection limit:** the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated level of confidence.
- **dose:** (toxicology) total mass of substance that is administered to a person.
- **dosage:** (toxicology) total mass of substance relative to some other quantity (e.g., mg/min, mg/area, mg/body mass).
- **dose confirmation sample:** a sample providing the mass of contaminant delivered during a test session. Contaminant delivery tools such as pipettors and syringes cannot be assumed to always perform at the manufacturer specifications, especially for viscous or highly volatile materials. The dose confirmation sample is used to provide confidence in the amount of agent applied to the sample by the tool during that test session. This value is needed for calculations such as percent neutralization or reduction in starting challenge that require accurate measurement of the starting contamination.
- **extraction:** the separation of a component from a mixture through selective solubility.
- **extraction efficiency:** the quantitative measurement of the solvent's ability to selectively solubilize (i.e., remove) the contaminant from the test material (e.g., coupon, contact sampler).
- **foam:** spongelike material used in the contact test to ensure contact mass pressure is evenly applied to the test surface.
- **hazard:** A condition with the potential to cause injury, illness, or death of personnel; damage to or loss of equipment or property; or mission degradation. (reference FM 3-11.9)
- **hydrolysis:** the chemical reaction of a compound with water.
- **hydrophilic:** having a strong affinity for water, tendency to dissolve, mix with or be wetted by water. Water droplets on hydrophilic surfaces will tend to spread towards a thin film.
- **hydrophobic:** lacking affinity for water, tending to repel and not absorb, combine with, or dissolve in water. Water droplets on a hydrophobic surface will tend to bead and remain sessile.
- **loading factor**: (vapor test) the ratio of the (contaminated) surface area / volume of the environment.
- **limit of detection:** LOD see *detection limit.*
- **limit of quantitation**: LOQ see *quantitation limit.*
- **mass balance:** the tracking and accounting for all mass in a system, expressed in percent as total mass collected / mass delivered. A mass balance less than 1 indicates loss in the system.
- **measurand:** the item being measured.
- **moderate condition:** test condition in middle of testing range that is the standard indoor office / laboratory condition at 19-21 °C and 50-60% relative humidity.
- **neutralization:** the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. (reference FM 3-11.9)

- **nonpersistent agent:** A chemical agent that when released dissipates and/or loses its ability to cause casualties after 10 to 15 minutes. (reference FM 3-11.9)
- **nonsorptive materials**: a material that does not retain a significant amount of contaminant by absorption though there may be minute quantity of adsorption. Sorption is dependent on material-contaminant interactions; a material that is sorptive with one contaminant may or may not be sorptive with another contaminant. Generally, bare metals and glass are nonsorptive materials for some agents.
- **operational decontamination**: decontamination carried out by an individual and/or a unit, restricted to specific parts of operationally essential equipment, material and/or working areas, in order to minimize contact and transfer hazards and to sustain operations. This may include decontamination of the individual beyond the scope of immediate decontamination, as well as decontamination of mission-essential spares and limited terrain decontamination. (reference FM 3-11.9)
- **panel:** *see coupon.*
- **percent efficacy (and calculation):** the measurement of the amount of contaminant removed from the material of interest as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **percent neutralization (and calculation)**: the measurement of the amount of contaminant reacted/neutralized as a result of the decontamination process. This value can be reported as calculated, approximated, or inferred.
- **quench compound:** substance used to chemically halt / deactivate the decontaminant active component to stop further reaction.
- **quantitation limit:** the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.
- **reduction in starting challenge (and calculation)**: the measurement of the mass of contaminant that has been removed from the material of interest. Calculation most often employed for the evaluation of physical removal, sorbent or pre-clean techniques. The value can be reported as calculated, approximated, or inferred.
- **Relative standard deviation (RSD)**: the standard deviation of a data set divided by the mean of the data set.
- **remaining agent:** the amount of contaminant present in / on the material of interest after the decontamination process has been conducted. This value is different from the residual agent in that no mass has been removed from the coupon by contact or vapor testing. This value cannot be used to calculate a contact- or vapor-hazard.
- **requirement levels**: the documented amount of permissible agent remaining after a decontaminant process, typically expressed as a vapor concentration (mg/m^3) or a surface concentration (mg/m^2).
- **residual agent**: the amount of contaminant present in / on the material of interest after the decontaminant process and hazard test has been conducted.
- **rinsate:** the collected rinse from the decontamination process. Sample may include residual decontaminant, agent, and agent byproducts in water.
- **room condition**: the temperature and relative humidity of the test location on the specific test day.

- **sessile drop**: a liquid droplet that is firmly attached to a surface. If the droplet significantly spreads across the surface it is better described as a thin film.
- **skin simulant:** material used in the contact test to estimate the contaminant transfer that may occur if the surface of interest was contacted (e.g., touched) by real skin. See test limitations regarding use for contact testing.
- **sorptive or porous materials**: a material that absorbs or adsorbs a contaminant. Sorption is dependent on material-agent interactions; a material that is sorptive with one agent may or may not be sorptive with another agent.
- **surface coverage**: usually in regard to contamination, this is the contaminated surface area of the test (coupon surface) area.
- **test condition:** for a specific agent–material-decon set the combined contamination, aging, decontaminant process, environmental and test sampling process (i.e., contact, vapor, remaining, residual) variables.
- **touch:** a contact test event is called a touch. A touch is characterized by the contact area, contact pressure, contact time duration and skin condition (wet versus dry). For the coupon test, the contact area is nominally the coupon area. The pressure is 0.7 to 1.0 psi which is equivalent to a 1 kg contact mass that is cylindrical with a 2 in. diameter. The contact time is typically 15 min.
- **toxic industrial chemicals:** chemicals developed or manufactured for use in industrial operations or research by industry, government, or academia. These chemicals are not primarily manufactured for the specific purpose of producing human casualties or rendering equipment, facilities, or areas dangerous for human use. (reference FM 3-11.9) These materials have an associated toxicity which is less than chemical agents; however, these materials are typically produced in large quantities and readily available.
- **toxic industrial materials:** Toxic Industrial Materials (TIMs) are “a specific type of industrial chemical i.e., one that has a LCt_{50} value (lethal concentration for 50% of the population multiplied by exposure time) less than 100,000 mg-min/m^3 in any mammalian species and is produced in quantities exceeding 30 tons per year at one production facility.” (reference NIJ Guide 100-00 Guide for the Selection of Chemical Agent and Toxic Industrial Material Detection Equipment for Emergency First Responders).
- **toxic load model**: the relationship used to describe exposure to a vapor concentration for a specified time that to induces a toxicological response. The relationship of $C^n t=k$ is used as specified in FM 3-11.9, compared to the use of Haber’s law of $Ct=k$.
- **uncertainty of measurement**: a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.
- **vapor chamber:** a dynamic vapor microchamber that fully encloses a coupon to enable vapor emission analysis. The chamber must facilitate the ability to control air flow and mixing, collect vapor samples, and measure environmental conditions such as temperature and relative humidity.
- **vapor cell**: a dynamic vapor enclosure that is placed over the surface to be tested for vapor emission analysis. The tested surface serves as one of the ‘walls’ of the enclosure. The use of a vapor cell is not within the methods described here.

- **vapor hazard:** a value specified in requirements documents, usually specified as a concentration (mg/m^3) that should have an accompanying exposure time. The value corresponds to an exposure that presents an acceptable risk level for unprotected personnel exposed to the vapor concentration. The toxic load model should be applied to calculate a vapor hazard.

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Sub-Appendix B: 2002 TOP Suggested Material and Contaminant List

A: Coupon Materials

Coupons are used in testing to represent specific surfaces of interest. The materials are to represent surfaces to be decontaminated such as vehicles, equipment and structures. The guidance from the 2002 TOP was that the test sponsor would identify the material set. According to the original document, "*a listing of assumed highest priority materials was developed by materiel developers based on the expected impact on mission/combat readiness, likelihood of being exposed to contamination, and cost to replace. In addition to the aforementioned prioritization that is focused on restoration of combat readiness and mission execution, compatibility with individual protective equipment is also proposed to be included among high priority materials to be evaluated.... Materials from aircraft, tactical and support vehicles, munitions, runways/flight decks, and individual protective equipment were deemed of primary importance and thus included in this listing.*" Although no specific approval was documented, the list is provided for reference as Part I. General research guidance is provided in Part II. The tester should document in the final report the materials used including any supporting documentation identifying who provided the list and any approvals received.

<u>PART I: Material listing and guidance from TOP 8-2-061 initial release 19 Nov. 2002</u>

(1) <u>List A</u>

(a) Chemical agent resistant coating (CARC) (tactical vehicles).

(b) Aircraft topcoat paint (aircraft).

(c) Low-infrared (IR) paints (aircraft & ships).

(d) Ship deck anti-skid.

(e) Polyurethane, epoxy, and alkyd paints (commercial vehicles).

(f) Aluminum alloy forged and cast (aircraft surfaces & structural members).

(g) Aluminum, oxidized aluminum (vehicle substrate surface).

(h) Stainless and high strength steel alloys (aircraft and engine structural members).

(i) Nickel based and other superalloys (aircraft and engine structural members).

(j) Carbon/stainless steels (vehicle, munitions substrate surface).

(k) Brass/bronze/copper and nickel alloys (munitions substrate surface).

(l) Composite and laminate materials (aircraft surface and structural members).

(m) Aircraft composites (aircraft).

(n) Tire rubber (aircraft, vehicles).

(o) Polycarbonates/Lexan® (aircraft canopy/window materials, tactical vehicles).

(p) Glass (commercial vehicles, tactical vehicles).

(q) Asphalt (runways and parking areas).

(r) Concrete (runways and parking areas).

(s) Standard tent, soft shelter material.

(2) List B

(a) Joint Service Lightweight Integrated Suit Technology (JSLIST).

(b) Battle dress overgarment.

(c) Butyl rubber (mask, gloves/boots).

(d) Silicon rubber (M40 mask).

(e) Cotton, polyester materials (uniform materials).

(f) Collective protection, soft shelter material.

(3) It is recommended that the A List materials be evaluated in terms of both decontamination effectiveness (effectiveness of a candidate decontaminant to decontaminate threat agents from a respective material) and materials compatibility (to determine the effects of the decontaminant on the surface being decontaminated).

(4) It is recommended that the B List materials be evaluated in terms of material compatibility and material performance only. Further, it is also recommended that the above list be recognized as a general guide to be used in the development of detailed test plans, and that the above list may be modified as deemed necessary to provide materials that are most generally representative of the categories of equipment mentioned within that list.

PART II: General Material Guidance

Research activities typically focus on the evaluation of a decontaminant performance across a range of materials differing in agent–material physical properties. The recommendation is a range of materials to evaluate decontaminant performance and penetration. Suggested materials include chemical agent resistant coating painted metal, bare metal (e.g., aluminum 7075 or stainless steels 304, 316), glass, polycarbonate and silicone.

B: Contaminants

Contaminants used in chemical decontamination testing can include chemical agents, chemical agent simulants, toxic industrial chemicals (TICs) and toxic industrial materials (TIMs). Chemical agent testing can only be performed at approved testing facilities. Chemical agent simulants are commonly used in scenarios or laboratories where live chemical agent testing cannot be performed. The contaminants used in testing can be specified by the customer, test director or requirements documents. Contaminants may include but are not limited to:

Chemical Agents: A chemical agent is a toxic chemical for use in military operations. A comprehensive listing of chemical agents can be found in Army Field Manual number 3-11.9. Commonly used chemical agents include:

- G-agents
- H-agents

- VX
- Thickened varieties

Chemical Agent Simulants: Chemical agent simulants are compounds with at least one similarity to live chemical agent, but are always lower in toxicity. These compounds do not contain all of the same physical and chemical properties of live agent, but are selected because of similarities in the main property of reference for a specific test. In some cases, simulant selection may be limited based on safety and environmental regulations. Commonly used chemical agent simulants include:

- G-agent simulants
- H-agent simulants
    - Methyl salicylate (MeS)
    - Chloroethyl phenyl sulfide (CEPS)
    - Chloroethyl ethyl sulfide (CEES)
- VX simulants

Toxic Industrial Materials: Toxic Industrial Chemicals (TICs) are chemical produced for industrial applications that are toxic to humans. According to the NIJ Guide 100-00 *Guide for the Selection of Chemical Agent and Toxic Industrial Material Detection Equipment for Emergency First Responders*: Toxic Industrial Materials (TIMs) are "a specific type of industrial chemical i.e., one that has a LCt_{50} value (lethal concentration for 50% of the population multiplied by exposure time) less than 100,000 mg-min/m^3 in any mammalian species and is produced in quantities exceeding 30 tons per year at one production facility." These materials are not as toxic as the chemical agents; however, these materials are typically produced in large quantities and readily available. According to the *International Task Force 25: Hazard from Industrial Chemicals Final Report* dated April 1998, TIMs are ranked by hazard index based on relative importance and hazard. A high hazard rating indicates a widely produced, stored or transported TIM that has high toxicity and is easily vaporized. A medium hazard rating indicates a TIM that may rank high in some categories but lower in others such as number of producers, physical state, or toxicity. A low hazard rating indicates that this TIM is not likely to be a hazard unless specific operational factors indicate otherwise. Not all TIMs require traditional decontamination procedures. The TIMs listing sorted by hazard rating is provided in Table 1. The TIMs of interest for decontaminant applications are the more persistent agents.

Table 1: TIMs Listed by Hazard Index

High	Medium	Low
Ammonia	Acetone cyanohydrin	Allyl isothiocyanate
Arsine	Acrolein	Arsenic trichloride
Boron trichloride	Acrylonitrile	Bromine
Boron trifluoride	Allyl alcohol	Bromine chloride
Carbon disulfide	Allylamine	Bromine pentafluoride
Chlorine	Allyl chlorocarbonate	Bromine trifluoride
Diborane	Boron tribromide	Carbonyl fluoride
Ethylene oxide	Carbon monoxide	Chlorine pentafluoride
Fluorine	Carbonyl sulfide	Chlorine trifluoride
Formaldehyde	Chloroacetone	Chloroacetaldehyde
Hydrogen bromide	Chloroacetonitrile	Chloroacetyl chloride
Hydrogen chloride	Chlorosulfonic acid	Crotonaldehyde
Hydrogen cyanide	Diketene	Cyanogen chloride
Hydrogen fluoride	1,2-Dimethylhydrazine	Dimethyl sulfate
Hydrogen sulfide	Ethylene dibromide	Diphenylmethane-4,4'-diisocyanate
Nitric acid, fuming	Hydrogen selenide	Ethyl chloroformate
Phosgene	Methanesulfonyl chloride	Ethyl chlorothioformate
Phosphorus trichloride	Methyl bromide	Ethyl phosphonothioic dichloride
Sulfur dioxide	Methyl chloroformate	Ethyl phosphonic dichloride
Sulfuric acid	Methyl chlorosilane	Ethyleneimine
Tungsten hexafluoride	Methyl hydrazine	Hexachlorocyclopentadiene
	Methyl isocyanate	Hydrogen iodide
	Methyl mercaptan	Iron pentacarbonyl
	Nitrogen dioxide	Isobutyl chloroformate
	Phosphine	Isopropyl chloroformate
	Phosphorus oxychloride	Isopropyl isocyanate
	Phosphorus pentafluoride	n-Butyl chloroformate
	Selenium hexafluoride	n-Butyl isocyanate
	Silicon tetrafluoride	Nitric oxide
	Stibine	n-Propyl chloroformate
	Sulfur trioxide	Parathion
	Sulfuryl chloride	Perchloromethyl mercaptan
	Sulfuryl fluoride	sec-Butyl chloroformate
	Tellurium hexafluoride	tert-Butyl isocyanate
	n-Octyl mercaptan	Tetraethyl lead
	Titanium tetracbloride	Tetraethyl pyrophosphate
	Trichloroacetyl chloride	Tetramethyl lead
	Trifluoroacetyl chloride	Toluene 2,4-diisocyanate
	Toluene 2,6-diisocyanate	

C: Decontaminants

The specific decontaminants for evaluation are dependent on the test objectives and specific test facility capability. Chemical decontaminants can be liquid-, solid- or vapor-phase and may contain a reactive functionality for neutralizing chemical contaminants. FM 3-11.5 Appendix C provides a detailed listing of decontaminants and their use. Liquid decontaminants can include but are not limited to solutions of sodium hydroxide, calcium hypochlorite (HTH), sodium hypochlorite (household bleach), DF-200, DS-2 and STB. Solid decontaminants can include but are not limited to reactive powders and sorbent wipes. Vaporous decontaminants can include vaporized hydrogen peroxide and chlorine dioxide. Physical removal, such as hot soapy water, fits the definition of decontaminant. Natural processes such as weathering and fire fit the definition of decontamination. Fire is typically not recommended if the item is to be recovered for potential reuse post decontamination.

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Sub-Appendix C: 2007 Low-Level Analytical Methods

TABLE OF CONTENTS

METHODS INTRODUCTION 388

METHOD A: LC-MS/MS METHOD FOR ULTRA LOW-LEVEL VX AND EA-2192 IDENTIFICATION (LCE VX_ULL.DAM) 389

METHOD B: LC-MS/MS METHOD FOR LOW-LEVEL VX AND EA-2192 IDENTIFICATION (LCE VX_LL.DAM) 401

METHOD C: LC-MS/MS METHOD FOR EMPA IDENTIFICATION (LCE EMPA.DAM) 413

METHOD D: GC/MSD METHOD FOR VX (GCE VX_DEANS.M) 421

METHOD E: GC-MS METHOD FOR LOW-LEVEL VX VAPOR SAMPLE ANALYSIS (GCV VX-DEANS.M) 431

METHOD F: GC-MS METHOD FOR LOW-LEVEL HD VAPOR SAMPLE ANALYSIS (GCV HDLL-DEANS.M) 441

METHOD G: GC-MS METHOD FOR HIGH-LEVEL HD VAPOR SAMPLE ANALYSIS (GCV HDHL-DEANS.M) 451

METHOD H: GC-MS METHOD FOR LOW-LEVEL GD VAPOR SAMPLE ANALYSIS (GCV GDLL-DEANS.M) 461

METHOD I: GC-MS METHOD FOR HIGH-LEVEL GD VAPOR SAMPLE ANALYSIS (GCV GDHL-DEANS.M) 471

METHOD J: GC/MS METHOD FOR LOW-LEVEL HD (GCE HD_DEANS.M) 481

METHOD K: GC/MS METHOD FOR LOW-LEVEL GD (GCE GD_DEANS.M) 491

METHOD L: GC-MS METHOD FOR TDG IDENTIFICATION (GCE TDG_DEANS.M) 501

METHOD M: LC-MS METHOD FOR HD SULFOXIDE IDENTIFICATION (LCE H-SULFIXOIDE.DAM) 511

METHOD N: GC-MS METHOD FOR HD SULFONE IDENTIFICATION (GCE H-SULFONE_DEANS.M) 519

METHOD O: GC-MS METHOD FOR GD-ACID IDENTIFICATION (GCE GD-ACID_DEANS.M) 532

Methods Introduction

CA06DEC407 was a DTRA JSTO funded effort designed to address the challenges associated with quantifying low-level residual agent to support decontaminant contact- and vapor-test evaluations. The program had three main objectives. The primary program objective was to develop improved analytical methods to enable the confident detection of low-level of chemical agents VX, HD and GD at published requirement levels. The lowest requirements at the time of this program used to establish the required detection limits were the Joint Platform Interior Decontamination (JPID) program 2003 and the Joint Service Sensitive Equipment Decontamination (JSSED) program 2005 requirement documents. An analytical method is an electronic file containing the settings the analytical equipment uses during operation. These settings are optimized for the specific objective (i.e., low-level VX). The analytical equipment is the hardware that uses the analytical methods. The second program objective was to establish methods for the detection of common agent byproducts that could form during decontaminant testing. The third program objective was to make the new methods available to establish uniformity in test procedures across testing locations. This document contains the set of test methods meeting all three project objectives.

This document is the compilation of methodology developed under program CA06DEC407. This document is formally published as an appendix to the final project technical report. The final technical report also contains the method development and demonstration, and cited references. The final technical is by Dr. Teri Lalain, et.al, and titled “Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations.” These methods are used to support decontaminant performance testing based on the following methods:

- West Desert Test Center, Dugway Proving Grounds, Test Operations Procedure (TOP) 8-2-061, Chemical and Biological Decontaminant Testing, 19 November 2002.
- Technical report by T. Lalain, et.al, titled “Development of the 2007 Chemical Decontaminant Source Document.”

Each method is documented as an individual method. The methods are constructed using standardized fields with all pertinent information. The ‘Analyte Concentration Range’ section provides an overview of the method target, the calibration range, calibration curve fitting model and weighting, limit of detection (LOD), limit of quantitation (LOQ), solvent and quantitation ion(s). The methods are identified as quantitative or qualitative. The program objective was byproduct identification. The byproduct methods as presented here are qualitative. All qualitative methods in this document can be quantitative if a second set of calibration standards using the byproduct are prepared and analyzed. The LOD and LOQ are calculated based on the laboratory evaluation of the final method. Each laboratory should recalculate these values based on their method performance. LOD and LOQ are a function of instrument sensitivity which can decay over time/use. Instrument sensitivity can often be restored by regular scheduled maintenance, thus illustrating the need for a regular maintenance schedule. It is anticipated that a laboratory can achieve the appearance of a better LOD and LOQ, especially for new equipment or following instrument maintenance. These values should be calculated over a period of time to determine the laboratory performance as discussed in the final technical report. The “Apparatus” section details the analytical equipment and standard preparation tools. The “Method Parameters” section provides the complete listing of instrumentation settings for the method.

METHOD A: LC-MS/MS METHOD FOR ULTRA LOW-LEVEL VX AND EA-2192 IDENTIFICATION (LCE VX_ULL.DAM)

ANALYTICAL METHOD

TITLE
Ultra-low level detection of VX and EA2192 in liquid extraction samples for chemical agent decontamination testing using an LC-MS/MS system.

AUTHORS
Matt Shue (SAIC)
Phil Smith, Ph.D. (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
VX, O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate, CAS 50782-69-9

EA2192, S-(2-Diisopropylaminoethyl) methylphosphonothioic acid, CAS 73207-98-4

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The primary purpose of this method is to detect and quantify ultra-low concentrations of the chemical agent VX in liquid extraction samples. The secondary purpose of this method is to screen liquid extraction samples for EA2192, a hydrolysis byproduct of VX. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately seven (7) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to exceed the low-level JPID ORD requirements as detailed in the Low-Level Test Execution and Resource Integration Plan. This method can detect VX solution concentrations from 0.05 to 10.0 ng/mL.

This method utilizes eight calibration standards at concentrations of 0.05, 0.1, 0.2, 0.5, 1.0, 2.5, 5, and 10 ng/ml VX. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in isopropyl alcohol. The mobile phase is a 50:50 mixture of the organic and aqueous phases. The organic phase consists of 95% acetonitrile, 5% de-ionized water, 0.1% formic acid, and 5 mM ammonium acetate. The aqueous phase consists of 95% de-ionized water, 5% acetonitrile, 0.1% formic acid, and 5 mM ammonium acetate. The method is conducted in an isocratic configuration.

The method performance for VX is:

- Quantitative Method
- Calibration range: 0.05 ng/mL to 10 ng/mL VX
- Calibration model: weighted linear regression
- Calibration weighting: 1/standard concentration

- Limit of Detection (LOD): 0.013 ng/mL
- Limit of Quantitation (LOQ): 0.039 ng/mL
- Sample Solvent: isopropyl alcohol
- Quant Ion Pair: VX 268.1 / 128

The method performance for EA2192 is as follows:
- Qualitative Method
- Sample Solvent: isopropyl alcohol
- Quant Ion Pair: EA-2192 240.1 / 128

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for liquid samples extracted with the solvent isopropyl alcohol (C_3H_8O; CAS #67-63-0) and containing the chemical agent VX and/or the VX byproduct EA2192. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on liquid chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Applied Biosystems API5000 Triple-quadrupole Mass Spectrometer equipped with the TurboV Ion Source. Sample introduction and chromatography are performed with an Agilent 1200 series liquid chromatograph (LC). Sample effluent is directed from the LC directly to the TurboV ion source of the API5000 MS. The system is fitted with an Agilent ZORBAX SB-C18 4.6 mm x 75 mm 3.5 μm column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Applied Biosystems and Agilent Technologies. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute VX standards prepared in high purity isopropyl alcohol solvent.

Volumetric glassware used for standard preparation should be Class A and meet the

specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method. The LC mobile phase solutions (aqueous and organic) are prepared in accordance with the method specifications.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"LCE VX_ULL"
ECBC Decon Sciences Team
408-LCE Method Summary

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INSTRUMENT CONTROL PARAMETERS:    LCE (1200 Series LC / API5000 MS)
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D:\Analyst Data\Projects\VX Analysis\VX Method Development\Acquisition
Methods

Acquisition Method Properties
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Comment:     LC/MS/MS Method (MRM)for ultra-low level VX in liquid
             extraction samples.  This method can also screen for the VX
             byproduct EA2192.

Synchronization Mode:        LC Sync
Auto-Equilibration:          Off
Acquisition Duration:        7min0sec
Number Of Scans:             667
Periods In File:             1
Acquisition Module:          Acquisition Method
Software version:            Analyst 1.4.2

==========================================================================
                             API5000 Mass Spec
==========================================================================

MS Method Properties:
Period 1:
--------------
Scans in Period:         667
Relative Start Time:     0.00 msec
Experiments in Period: 1

Period 1  Experiment     1:
----------------------------
Scan Type:               MRM (MRM)
Polarity:                Positive
Scan Mode:               N/A
Ion Source:              Turbo Spray
Resolution Q1:           Unit
Resolution Q3:           High
Intensity Thres.:        0.00 cps
Settling Time:           0.0000 msec
MR Pause:                5.0070 msec
MCA:                     No
Step Size:               0.00 amu
```

```
@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            128.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            167.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            139.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            128.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            162.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            139.00            100.00

Parameter Table(Period 1  Experiment   1):
CUR:         15.00
GS1:         50.00
GS2:         55.00
IS:          5500.00
TEM:         550.00
ihe:         ON
CAD:         3.00
DP           60.00
EP           10.00
CE           25.00
CXP          12.00


END OF INSTRUMENT CONTROL PARAMETERS
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AGILENT 1200 SERIES LC PARAMETERS

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Agilent LC Pump Method Properties

Pump Model:	Agilent 1200 Binary Pump
Minimum Pressure (psi):	0.0
Maximum Pressure (psi):	5801.0
Dead Volume (µl):	40.0
Maximum Flow Ramp (ml/min^2):	100.0
Maximum Pressure Ramp (psi/sec):	290.0

Step Table:

@Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	1.00	200	50.0	50.0
1	7.00	200	50.0	50.0

Left Compressibility:	50.0
Right Compressibility:	115.0
Left Dead Volume (µl):	40.0
Right Dead Volume (µl):	40.0
Left Stroke Volume (µl):	-1.0
Right Stroke Volume (µl):	-1.0
Left Solvent:	A2
Right Solvent:	B2

Agilent Autosampler Properties

Autosampler Model:	Agilent 1200 High Performance Autosampler
Syringe Size (µl):	100
Injection Volume (µl):	4.00
Draw Speed (µl/min):	200.0
Eject Speed (µl/min):	200.0
Needle Level (mm):	0.00
Temperature Control	Not Used
Wash Location:	Wash Vial
Wash Cycles (1 - 5):	2
Wash Vial Number:	1
Wash Rack Number:	1

Automatic Delay Volume Reduction	Not Used
Equilibration Time (sec):	2
Enable Vial/Well Bottom Sensing	No
Use Custom Injector Program	No

Agilent Column Oven Properties

Left Temperature (°C):	25.00
Right Temperature (°C):	25.00
Temperature Tolerance +/- (°C):	10.00

Start Acquisition	
Tolerance +/- (°C):	5.00
Time Table	(Not Used)
Column Switching Valve	Installed
Position for first	
sample in the batch:	Left

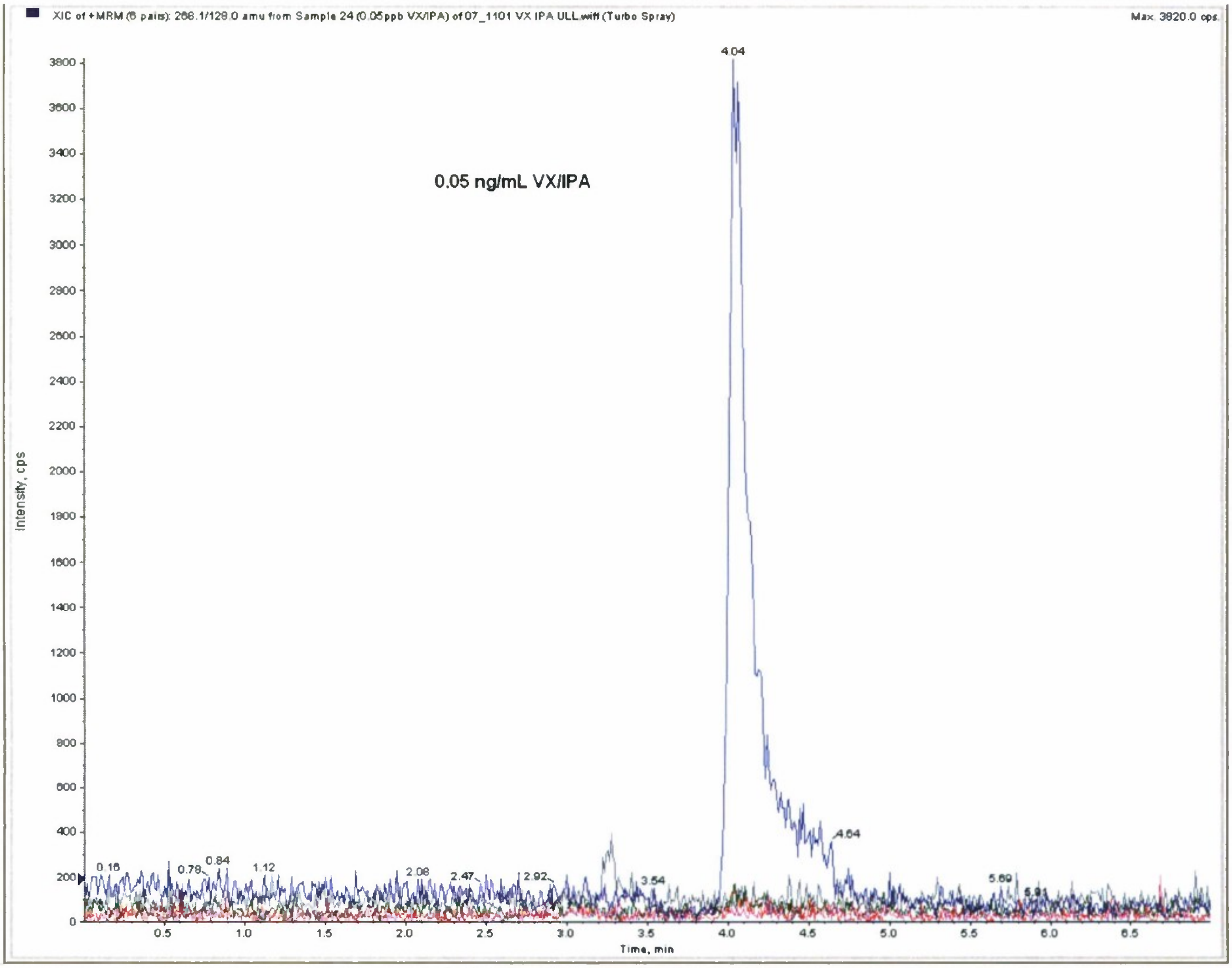
Use same position for all samples in the batch

Column Type:
Agilent ZORBAX
SB-C18
PN: 866953-902
SN: USDZ010845
4.6mm x 75mm 3.5µm

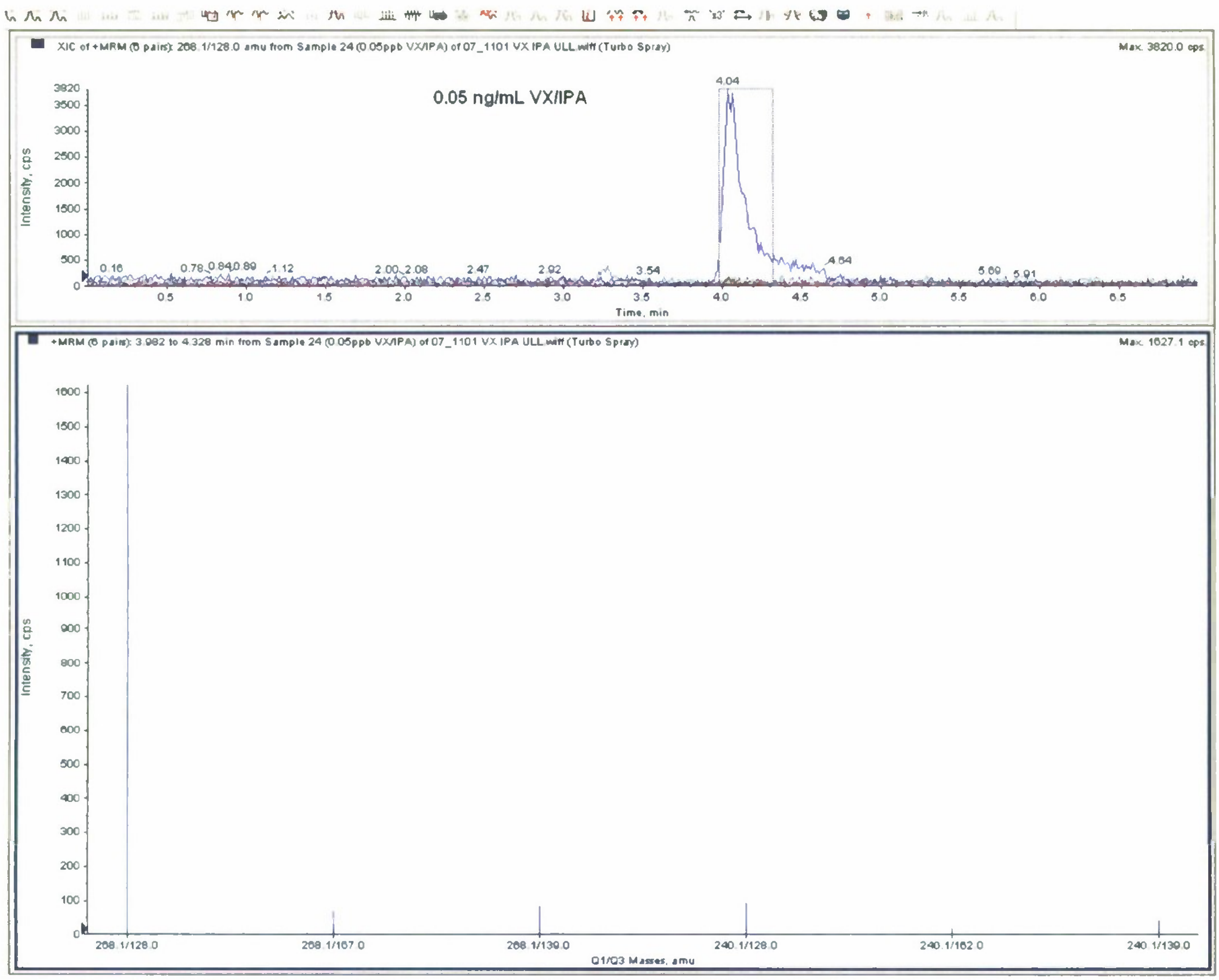
Mobile Phase
Aqueous:
95% dH20
5% Acetonitrile
0.1% Formic Acid
5mM Ammonium Acetate

Organic:
95% Acetonitrile
5% dH20
0.1% Formic Acid
5mM Ammonium Acetate

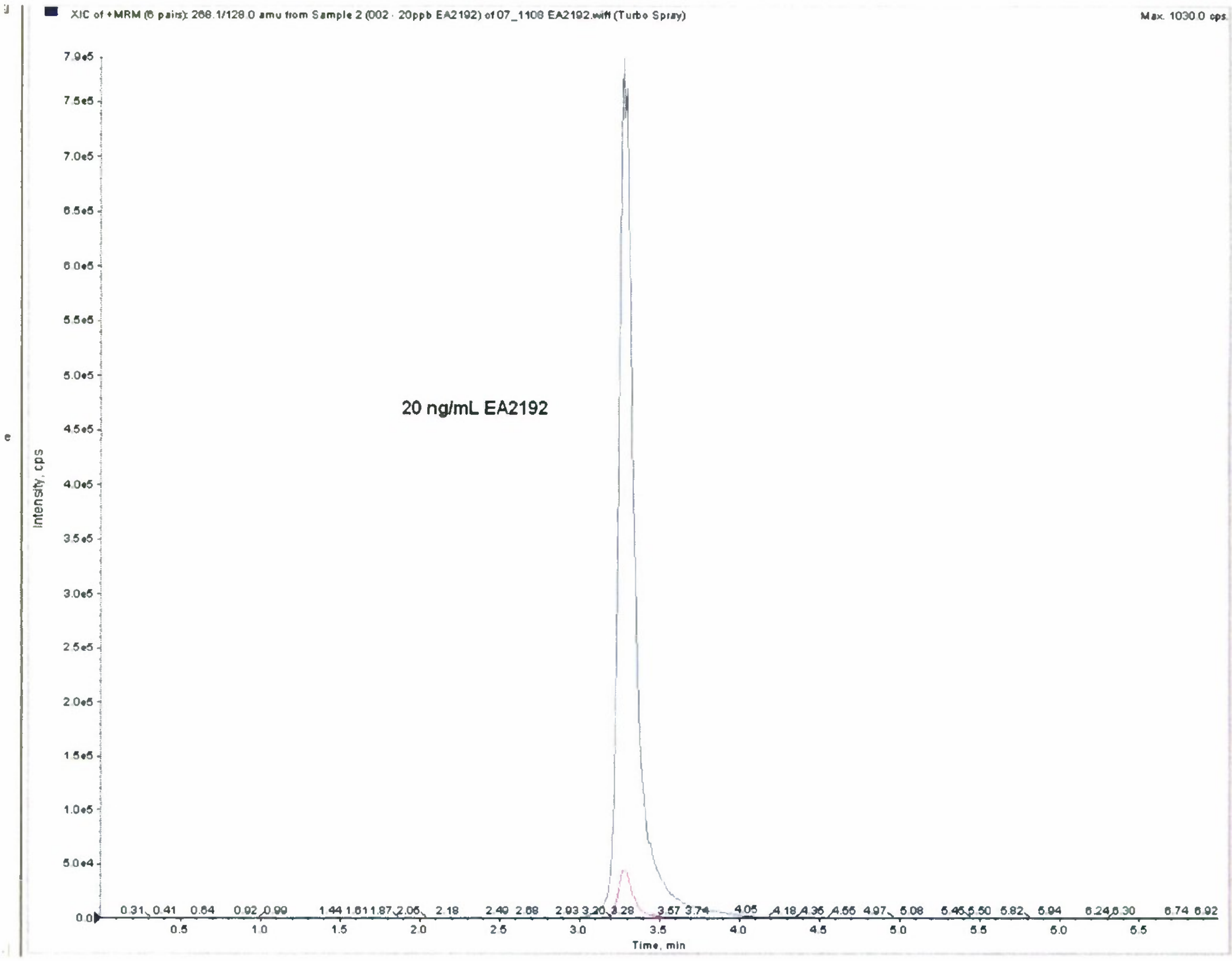
VX Chromatogram - 408-LCE DATA ANALYSIS



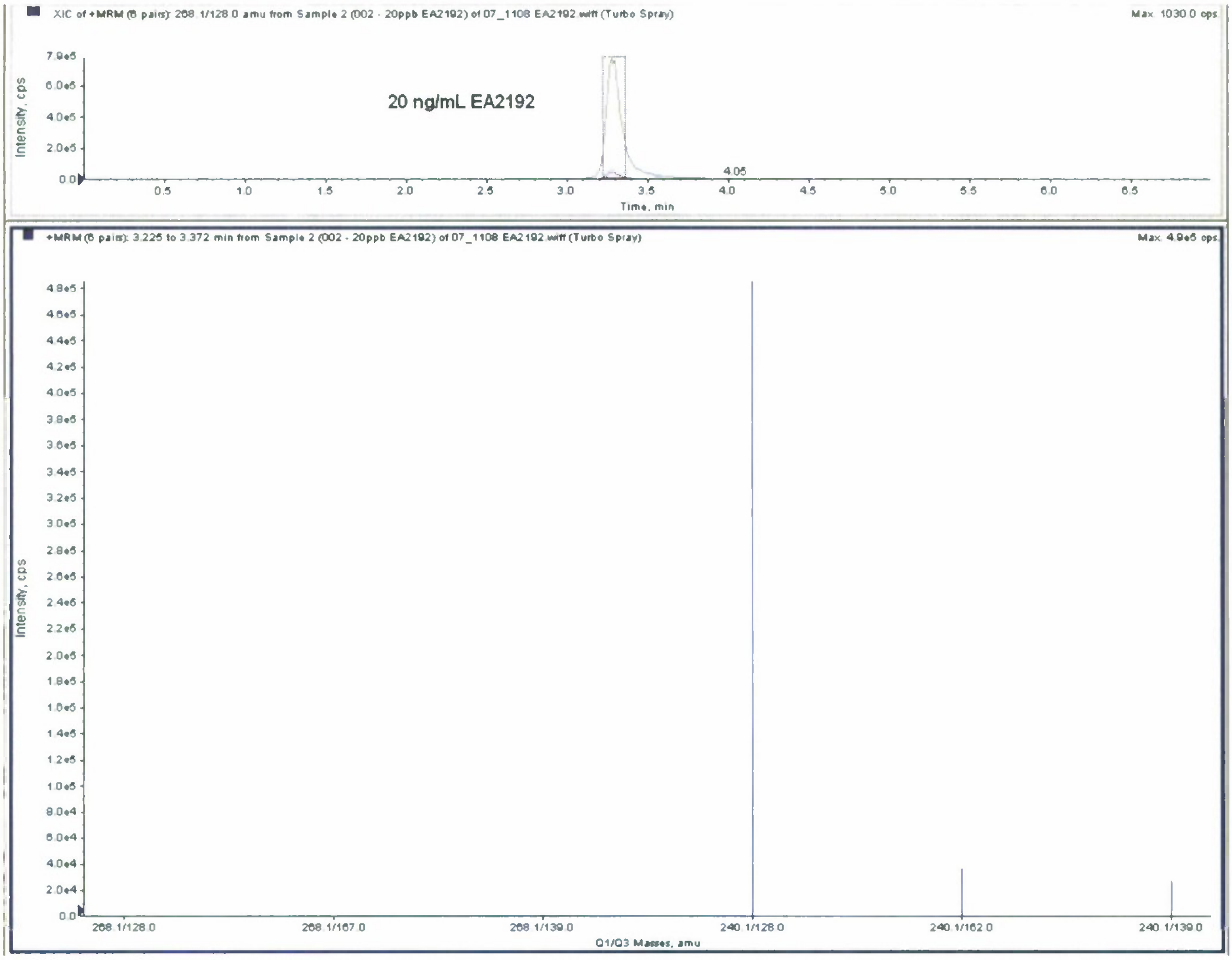
VX MS/MS Spectrum - 408-LCE DATA ANALYSIS



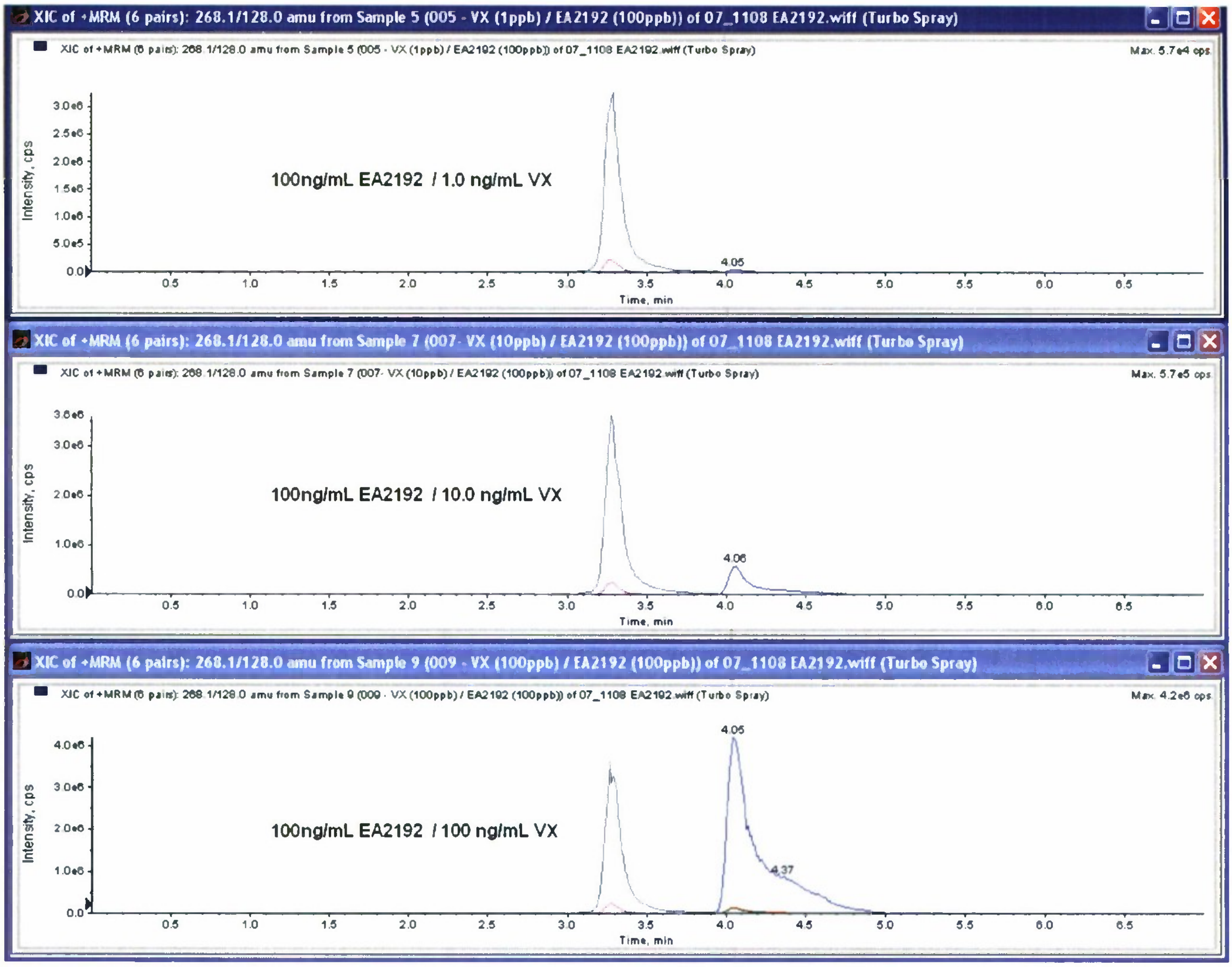
EA2192 Chromatogram - 408-LCE DATA ANALYSIS



EA2192 MS/MS Spectrum - 408-LCE DATA ANALYSIS



VX/EA2192 - 408-LCE DATA ANALYSIS



METHOD B: LC-MS/MS METHOD FOR LOW-LEVEL VX AND EA-2192 IDENTIFICATION (LCE VX_LL.DAM)

ANALYTICAL METHOD

TITLE
Low level detection of VX and EA2192 in liquid extraction samples for chemical agent decontamination testing using an LC-MS/MS system.

AUTHORS
Matt Shue (SAIC)
Phil Smith, Ph.D. (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
VX, O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate, CAS 50782-69-9

EA2192, S-(2-Diisopropylaminoethyl) methylphosphonothioic acid, CAS 73207-98-4

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The primary purpose of this method is to detect and quantify low level concentrations of the chemical agent VX in liquid extraction samples. The secondary purpose of this method is to screen liquid extraction samples for EA2192, a hydrolysis byproduct of VX. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately seven (7) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed as a complementary method to the Ultra-low level method (LCE VX_ULL.dam) to allow for VX decontamination testing at levels at or slightly higher concentrations than the ultra-low-level method. As a complementary method, this method can detect VX solution concentrations from 10.0 to 750 ng/mL.

This method utilizes seven calibration standards at concentrations of 10, 25, 50, 100, 250, 500, and 750 ng/ml VX. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in isopropyl alcohol. The mobile phase is a 50:50 mixture of the organic and aqueous phases. The organic phase consists of 95% acetonitrile, 5% de-ionized water, 0.1% formic acid, and 5 mM ammonium acetate. The aqueous phase consists of 95% de-ionized water, 5% acetonitrile, 0.1% formic acid, and 5 mM ammonium acetate. The method is conducted in an isocratic configuration.

The method performance for VX is as follows:

- Quantitative Method
- Calibration range: 10 to 750 ng/mL VX

- Calibration model: quadratic calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 1.41 ng/mL
- Limit of Quantitation (LOQ): 4.27 ng/mL
- Sample Solvent: isopropyl alcohol
- Quant Ion: VX 268.1 / 128

The method performance for EA2192 is as follows:

- Qualitative Method
- Sample Solvent: isopropyl alcohol
- Quant Ion: EA-2192 240.1 / 128

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for liquid samples extracted with the solvent isopropyl alcohol (C_3H_8O; CAS #67-63-0) and containing the chemical agent VX and/or the VX byproduct EA2192. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on liquid chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Applied Biosystems API5000 Triple-quadrupole Mass Spectrometer equipped with the TurboV Ion Source. Sample introduction and chromatography are performed with an Agilent 1200 series liquid chromatograph (LC). Sample effluent is directed from the LC directly to the TurboV ion source of the API5000 MS. The system is fitted with an Agilent ZORBAX SB-C18 4.6 mm x 75 mm 3.5 µm column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Applied Biosystems and Agilent Technologies. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute VX standards prepared in high purity isopropyl alcohol

solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method. The LC mobile phase solutions (aqueous and organic) are prepared in accordance with the method specifications.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                              "LCE VX_LL"
                       ECBC Decon Sciences Team
                       408-LCE Method Summary

   INSTRUMENT CONTROL PARAMETERS:    LCE (1200 Series LC / API5000 MS)
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D:\Analyst Data\Projects\VX Analysis\VX Method Development\Acquisition
Methods

Acquisition Method Properties
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Comment:    LC/MS/MS Method (MRM) for low level VX in liquid extraction
            samples.  This method can also screen for the VX byproduct
            EA2192.

Synchronization Mode:        LC Sync
Auto-Equilibration:          Off
Acquisition Duration:        7min0sec
Number Of Scans:             667
Periods In File:             1
Acquisition Module:          Acquisition Method
Software version:            Analyst 1.4.2

=========================================================================
                            API5000 Mass Spec
=========================================================================

MS Method Properties:
Period 1:
--------------
Scans in Period:       667
Relative Start Time:   0.00 msec
Experiments in Period: 1

Period 1  Experiment   1:
----------------------------
Scan Type:             MRM (MRM)
Polarity:              Positive
Scan Mode:             N/A
Ion Source:            Turbo Spray
Resolution Q1:         Unit
Resolution Q3:         High
Intensity Thres.:      0.00 cps
Settling Time:         0.0000 msec
MR Pause:              5.0070 msec
MCA:                   No
Step Size:             0.00 amu
```

```
@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            128.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            167.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
268.15            139.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            128.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            162.00            100.00

@Q1 Mass (amu)    Q3 Mass (amu)     Dwell(msec) Param Start Stop
240.10            139.00            100.00

Parameter Table(Period 1  Experiment   1):
CUR:         15.00
GS1:         40.00
GS2:         0.00
IS:          5500.00
TEM:         0.00
ihe:         ON
CAD:         6.00
DP           60.00
EP           10.00
CE           25.00
CXP          12.00


END OF INSTRUMENT CONTROL PARAMETERS
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AGILENT 1200 SERIES LC PARAMETERS

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Agilent LC Pump Method Properties

Pump Model:	Agilent 1200 Binary Pump
Minimum Pressure (psi):	0.0
Maximum Pressure (psi):	5801.0
Dead Volume (µl):	40.0
Maximum Flow Ramp (ml/min^2):	100.0
Maximum Pressure Ramp (psi/sec):	290.0

Step Table:

@Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	1.00	200	50.0	50.0
1	7.00	200	50.0	50.0

Left Compressibility:	50.0
Right Compressibility:	115.0
Left Dead Volume (µl):	40.0
Right Dead Volume (µl):	40.0
Left Stroke Volume (µl):	-1.0
Right Stroke Volume (µl):	-1.0
Left Solvent:	A2
Right Solvent:	B2

Agilent Autosampler Properties

Autosampler Model:	Agilent 1200 High Performance Autosampler
Syringe Size (µl):	100
Injection Volume (µl):	4.00
Draw Speed (µl/min):	200.0
Eject Speed (µl/min):	200.0
Needle Level (mm):	0.00
Temperature Control	Not Used
Wash Location:	Wash Vial
Wash Cycles (1 - 5):	2
Wash Vial Number:	1
Wash Rack Number:	1

Automatic Delay Volume Reduction	Not Used
Equilibration Time (sec):	2
Enable Vial/Well Bottom Sensing	No
Use Custom Injector Program	No

Agilent Column Oven Properties

Left Temperature (°C):	25.00
Right Temperature (°C):	25.00
Temperature Tolerance +/- (°C):	10.00

Start Acquisition	
Tolerance +/- (°C):	5.00
Time Table	(Not Used)
Column Switching Valve	Installed
Position for first sample in the batch:	Left

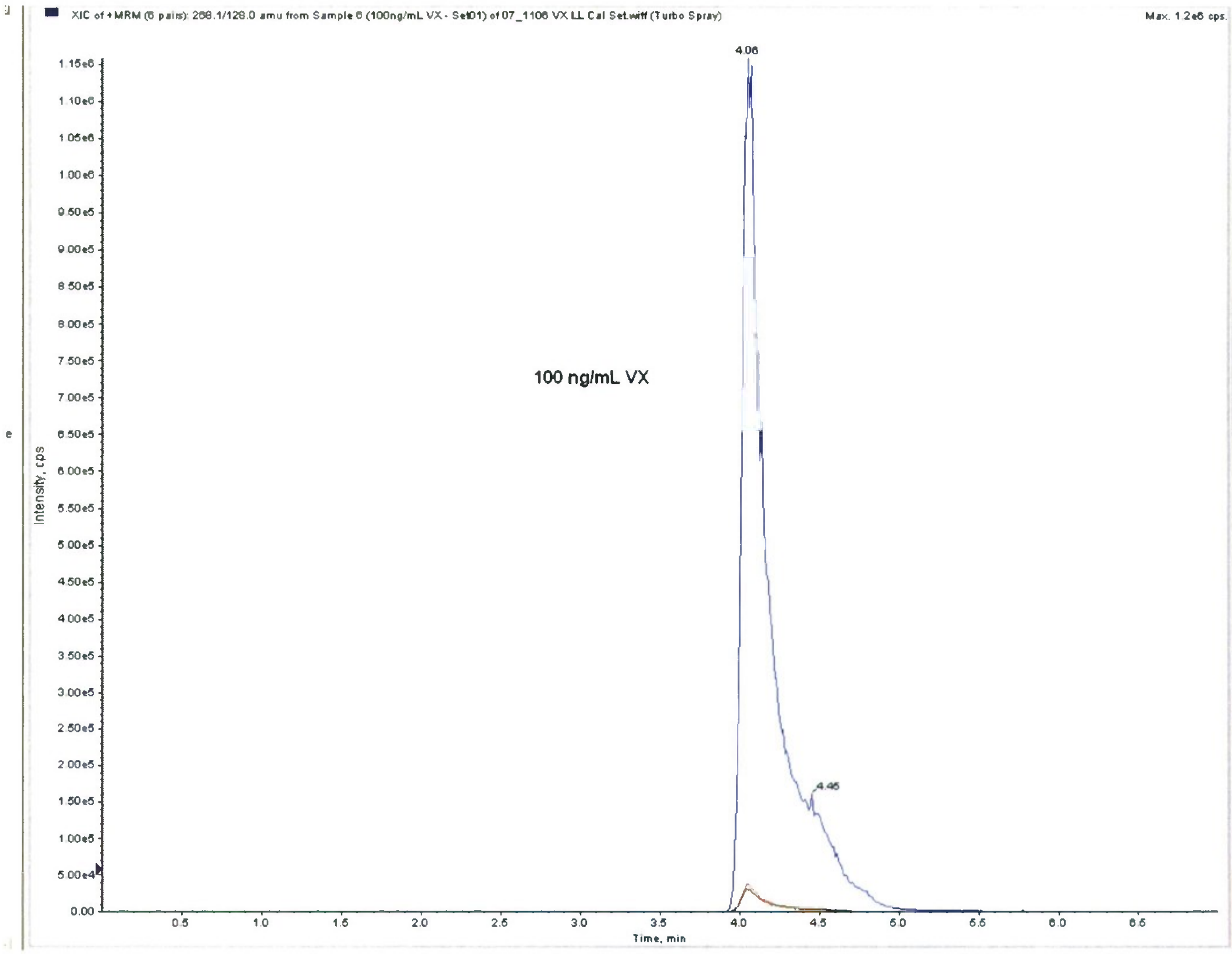
Use same position for all samples in the batch

Column Type:
Agilent ZORBAX
SB-C18
PN: 866953-902
SN: USDZ010845
4.6mm x 75mm 3.5µm

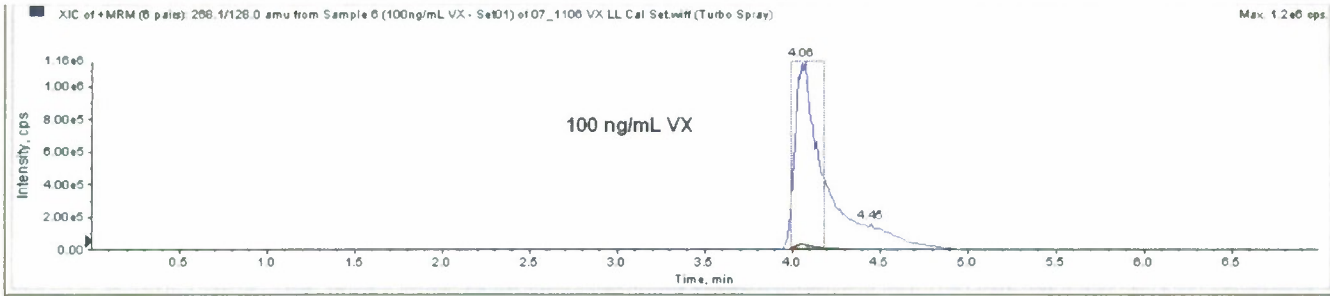
Mobile Phase
Aqueous:
95% dH20
5% Acetonitrile
0.1% Formic Acid
5mM Ammonium Acetate

Organic:
95% Acetonitrile
5% dH20
0.1% Formic Acid
5mM Ammonium Acetate

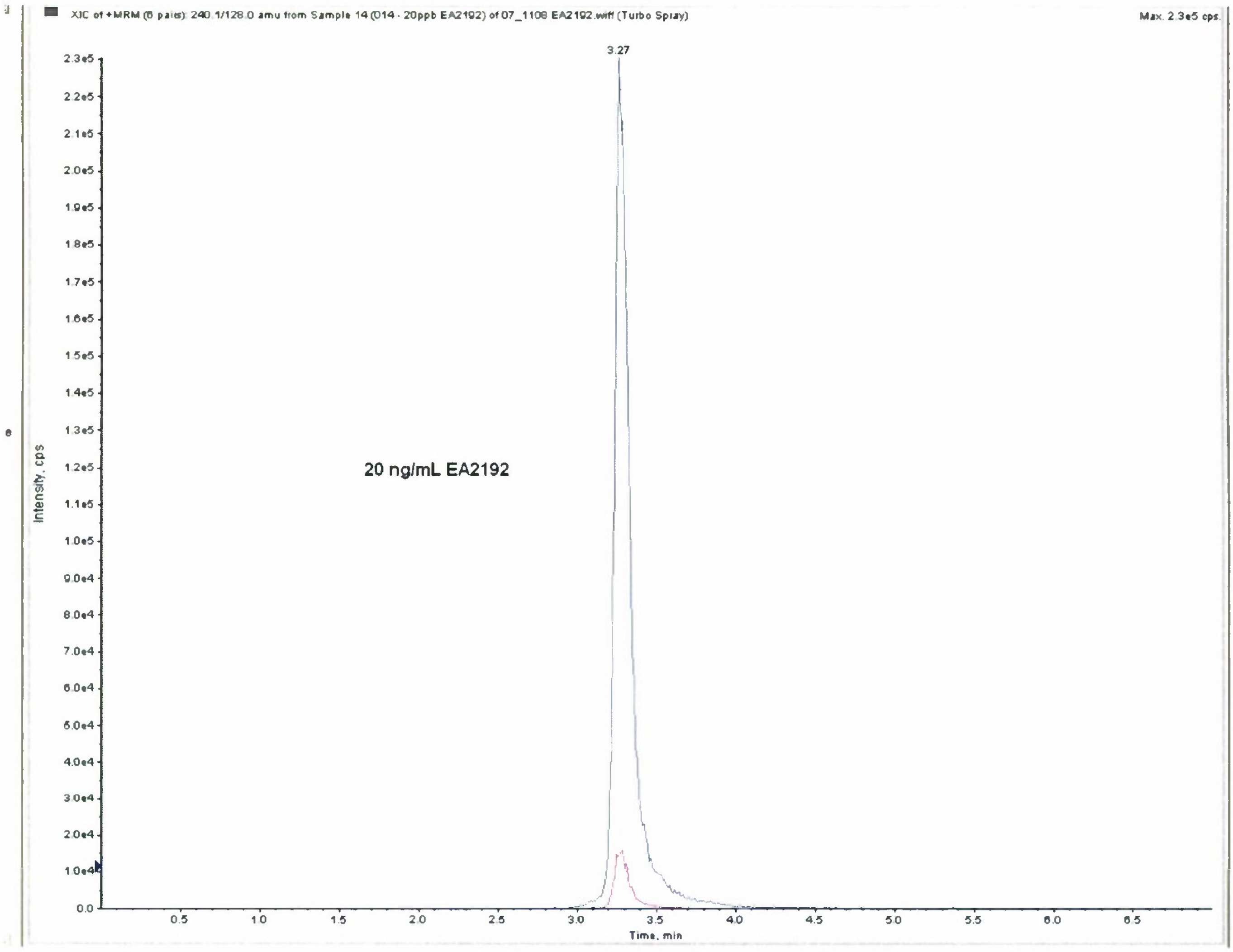
VX Chromatogram - 408-LCE DATA ANALYSIS



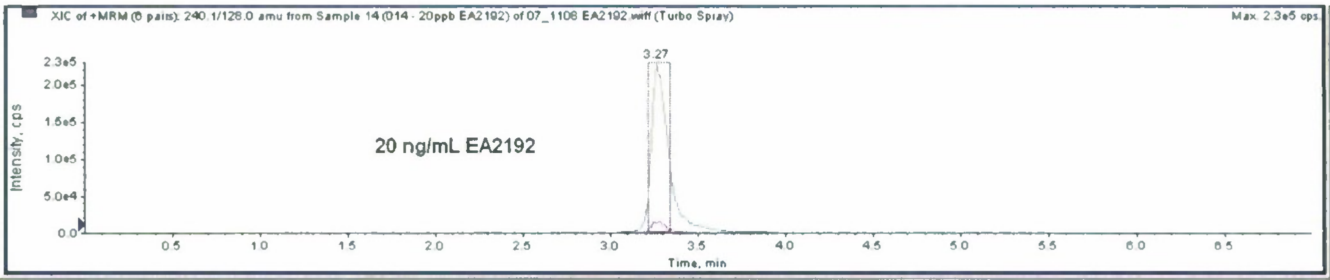
VX MS/MS Spectrum - 408-LCE DATA ANALYSIS

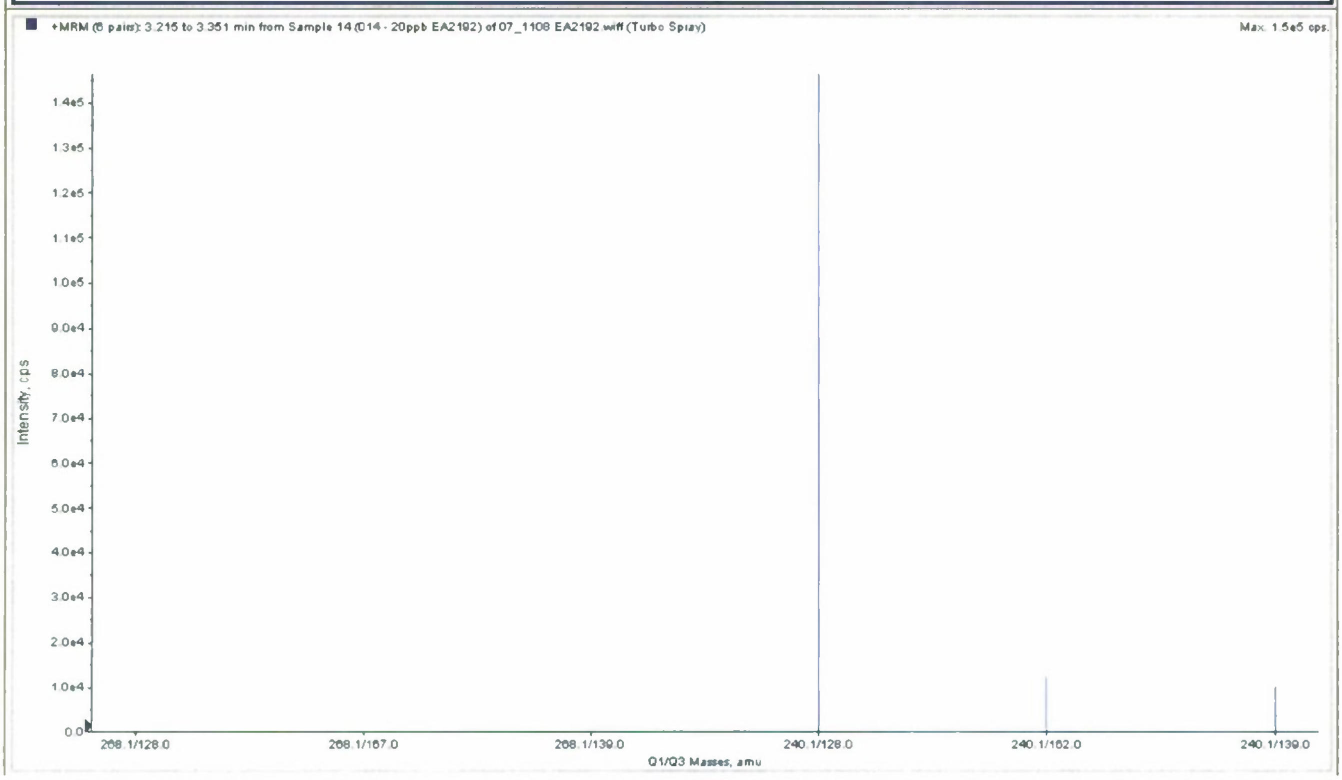


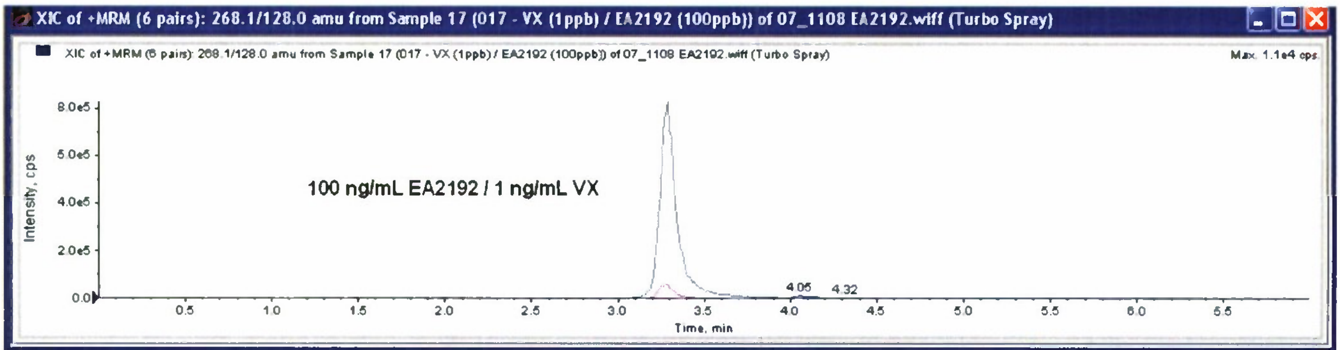
EA2192 Chromatogram - 408-LCE DATA ANALYSIS

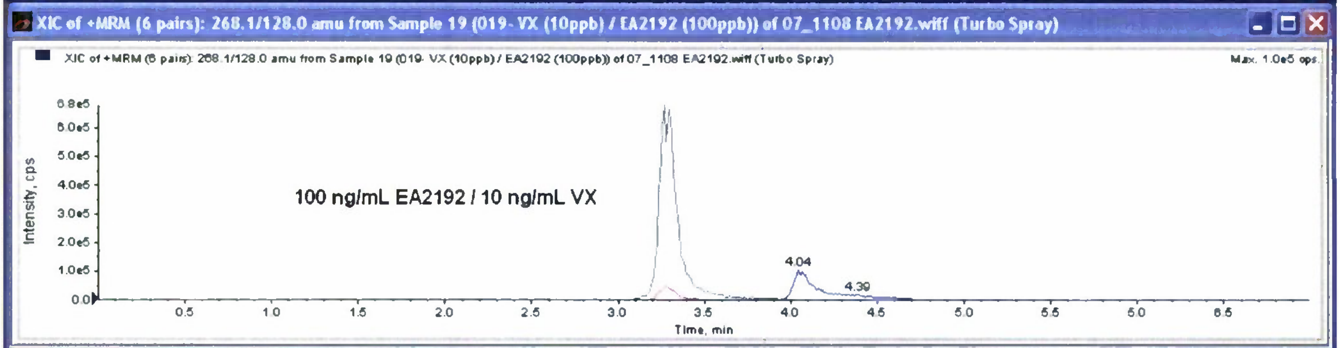


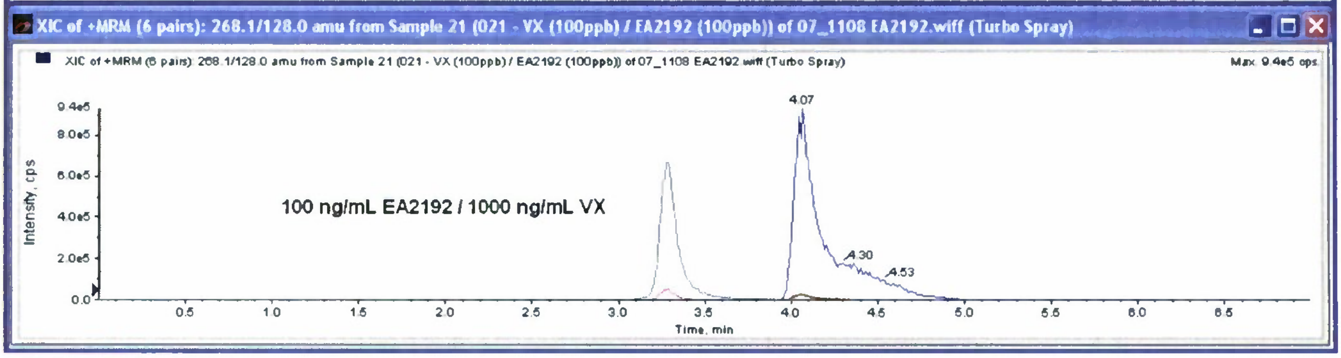
EA2192 MS/MS Spectrum - 408-LCE DATA ANALYSIS






XIC of +MRM (6 pairs): 268.1/128.0 amu from Sample 17 (017 - VX (1ppb) / EA2192 (100ppb)) of 07_1108 EA2192.wiff (Turbo Spray)
Max. 1.1e4 cps
Intensity, cps
Time, min
100 ng/mL EA2192 / 1 ng/mL VX
4.05
4.32


XIC of +MRM (6 pairs): 268.1/128.0 amu from Sample 19 (019- VX (10ppb) / EA2192 (100ppb)) of 07_1108 EA2192.wiff (Turbo Spray)
Max. 1.0e5 cps
Intensity, cps
Time, min
100 ng/mL EA2192 / 10 ng/mL VX
4.04
4.39


XIC of +MRM (6 pairs): 268.1/128.0 amu from Sample 21 (021 - VX (100ppb) / EA2192 (100ppb)) of 07_1108 EA2192.wiff (Turbo Spray)
Max. 9.4e5 cps
Intensity, cps
Time, min
100 ng/mL EA2192 / 1000 ng/mL VX
4.07
4.30
4.53

METHOD C: LC-MS/MS METHOD FOR EMPA IDENTIFICATION (LCE EMPA.DAM)

ANALYTICAL METHOD

TITLE
Detection of EMPA, a hydrolysis product of VX, in liquid extraction samples from chemical agent decontamination testing using an LC-MS/MS system.

AUTHORS
Matt Shue (SAIC)
Phil Smith, Ph.D. (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
EMPA, Ethyl methylphosphonate, CAS 1832-53-7

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect Ethyl methyphosphonate (EMPA). EMPA is a hydrolysis byproduct of the chemical agent VX. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately seven (7) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to screen for a VX byproduct, EMPA. The approximate concentration range for this method is from 5.0 to 500 ng/mL.

The method performance for EMPA is as follows:

- Qualitative Method
- Sample Solvent: isopropyl alcohol
- Quant Ion: 123 / 95

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent isopropyl alcohol (C_3H_8O; CAS #67-63-0) and suspected to contain the VX byproduct EMPA. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT
This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method

should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on liquid chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Applied Biosystems API5000 Triple-quadrupole Mass Spectrometer equipped with the TurboV Ion Source. Sample introduction and chromatography are performed with an Agilent 1200 series liquid chromatograph (LC). Sample effluent is directed from the LC directly to the TurboV ion source of the API5000 MS. The system is fitted with a Agilent ZORBAX SB-C18 4.6 mm x 75 mm 3.5 µm column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Applied Biosystems and Agilent Technologies. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include a dilute standard of EMPA prepared in high purity isopropyl alcohol solvent between the working concentration ranges of this method.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method. The LC mobile phase solutions (aqueous and organic) are prepared in accordance with the method specifications.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                          "LCE EMPA"
                   ECBC Decon Sciences Team
                    408-LCE Method Summary


   INSTRUMENT CONTROL PARAMETERS:    LCE (1200 Series LC / API5000 MS)
   -----------------------------------------------------------------

D:\Analyst Data\Projects\VX Analysis\VX Method Development\Acquisition
Methods

Acquisition Method Properties
------- --------------------

Comment:   LC/MS/MS Method (MRM)for EMPA.

Synchronization Mode:        LC Sync
Auto-Equilibration:          Off
Acquisition Duration:        7min0sec
Number Of Scans:             683
Periods In File:             1
Acquisition Module:          Acquisition Method
Software version:            Analyst 1.4.2

=======================================================================
                             API5000 Mass Spec
```

```
==========================================================================

MS Method Properties:
Period 1:
--------------
Scans in Period:       683
Relative Start Time:   0.00 msec
Experiments in Period: 1

Period 1  Experiment   1:
----------------------------
Scan Type:             MRM (MRM)
Polarity:              Negative
Scan Mode:             N/A
Ion Source:            Turbo Spray
Resolution Q1:         Unit
Resolution Q3:         High
Intensity Thres.:      0.00 cps
Settling Time:         0.0000 msec
MR Pause:              5.0070 msec
MCA:                   No
Step Size:             0.00 amu


@Q1 Mass (amu)    Q3 Mass (amu)    Dwell(msec) Param Start Stop
123.00            95.00            200.00

@Q1 Mass (amu)    Q3 Mass (amu)    Dwell(msec) Param Start Stop
123.00            79.00            200.00

@Q1 Mass (amu)    Q3 Mass (amu)    Dwell(msec) Param Start Stop
123.00            77.00            200.00

Parameter Table(Period 1  Experiment   1):
CUR:         -10.00
GS1:         50.00
GS2:         55.00
TEM:         500.00
ihe:         ON
CAD:         6.00
IS:          -4200.00
DP           -100.00
EP           -10.00
CE           -25.00
CXP          -15.00


END OF INSTRUMENT CONTROL PARAMETERS
------------------------------------

==========================================================================
                     AGILENT 1200 SERIES LC PARAMETERS
==========================================================================
```

Agilent LC Pump Method Properties

Pump Model:	Agilent 1200 Binary Pump
Minimum Pressure (psi):	0.0
Maximum Pressure (psi):	5801.0
Dead Volume (µl):	40.0
Maximum Flow Ramp (ml/min²):	100.0
Maximum Pressure Ramp (psi/sec):	290.0

Step Table:

@Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	1.00	200	50.0	50.0
1	7.00	200	50.0	50.0

Left Compressibility:	50.0
Right Compressibility:	115.0
Left Dead Volume (µl):	40.0
Right Dead Volume (µl):	40.0
Left Stroke Volume (µl):	-1.0
Right Stroke Volume (µl):	-1.0
Left Solvent:	A2
Right Solvent:	B2

Agilent Autosampler Properties

Autosampler Model:	Agilent 1200 High Performance Autosampler
Syringe Size (µl):	100
Injection Volume (µl):	4.00
Draw Speed (µl/min):	200.0
Eject Speed (µl/min):	200.0
Needle Level (mm):	0.00
Temperature Control	Not Used
Wash Location:	Wash Vial
Wash Cycles (1 - 5):	2
Wash Vial Number:	1
Wash Rack Number:	1

Automatic Delay Volume Reduction	Not Used
Equilibration Time (sec):	2
Enable Vial/Well Bottom Sensing	No
Use Custom Injector Program	No

Agilent Column Oven Properties

Left Temperature (°C):	25.00
Right Temperature (°C):	25.00
Temperature Tolerance +/- (°C):	10.00
Start Acquisition Tolerance +/- (°C):	5.00
Time Table	(Not Used)
Column Switching Valve	Installed
Position for first	

sample in the batch: Left

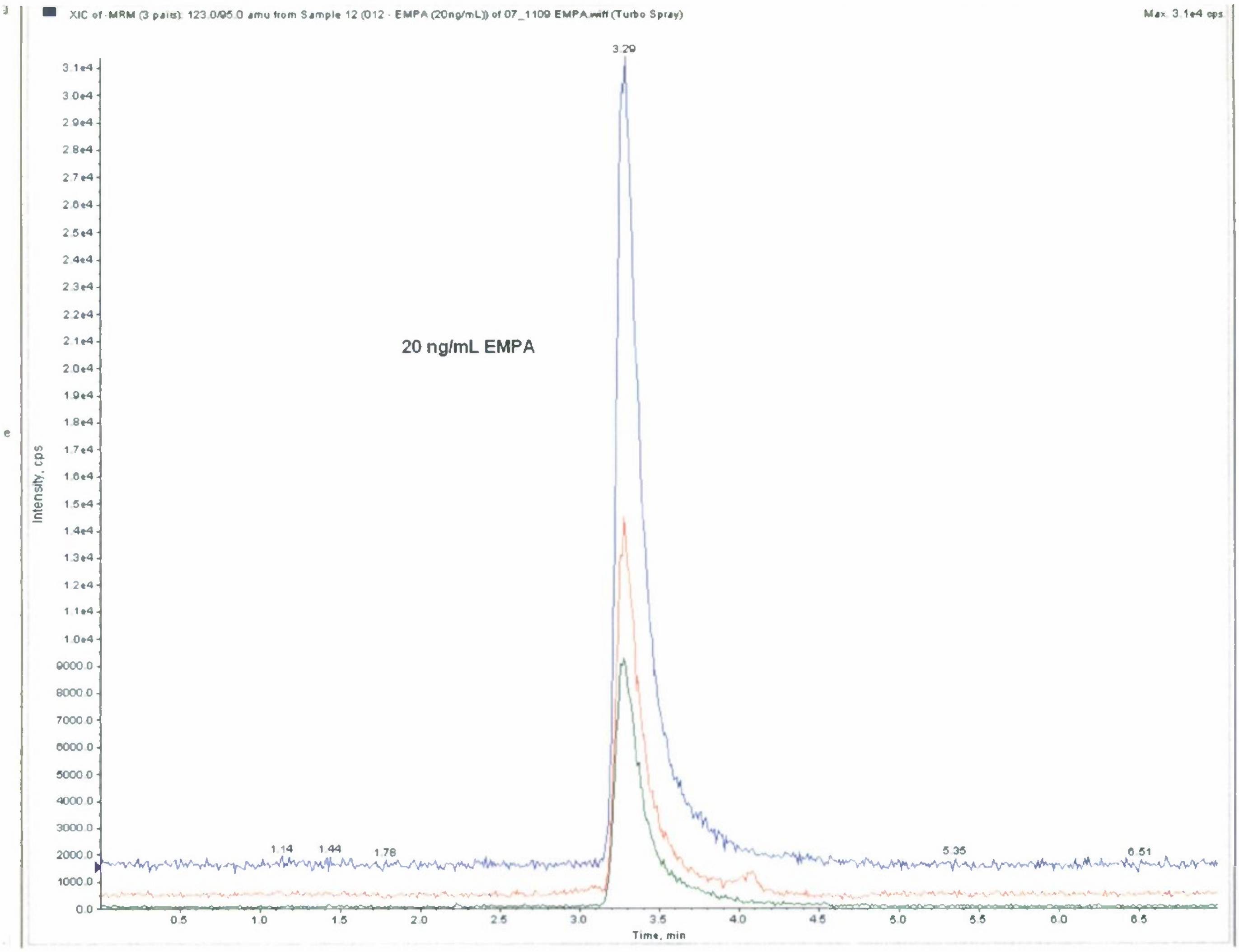
Use same position for all samples in the batch

Column Type:
Agilent ZORBAX
SB-C18
PN: 866953-902
SN: USDZ010845
4.6mm x 75mm 3.5µm

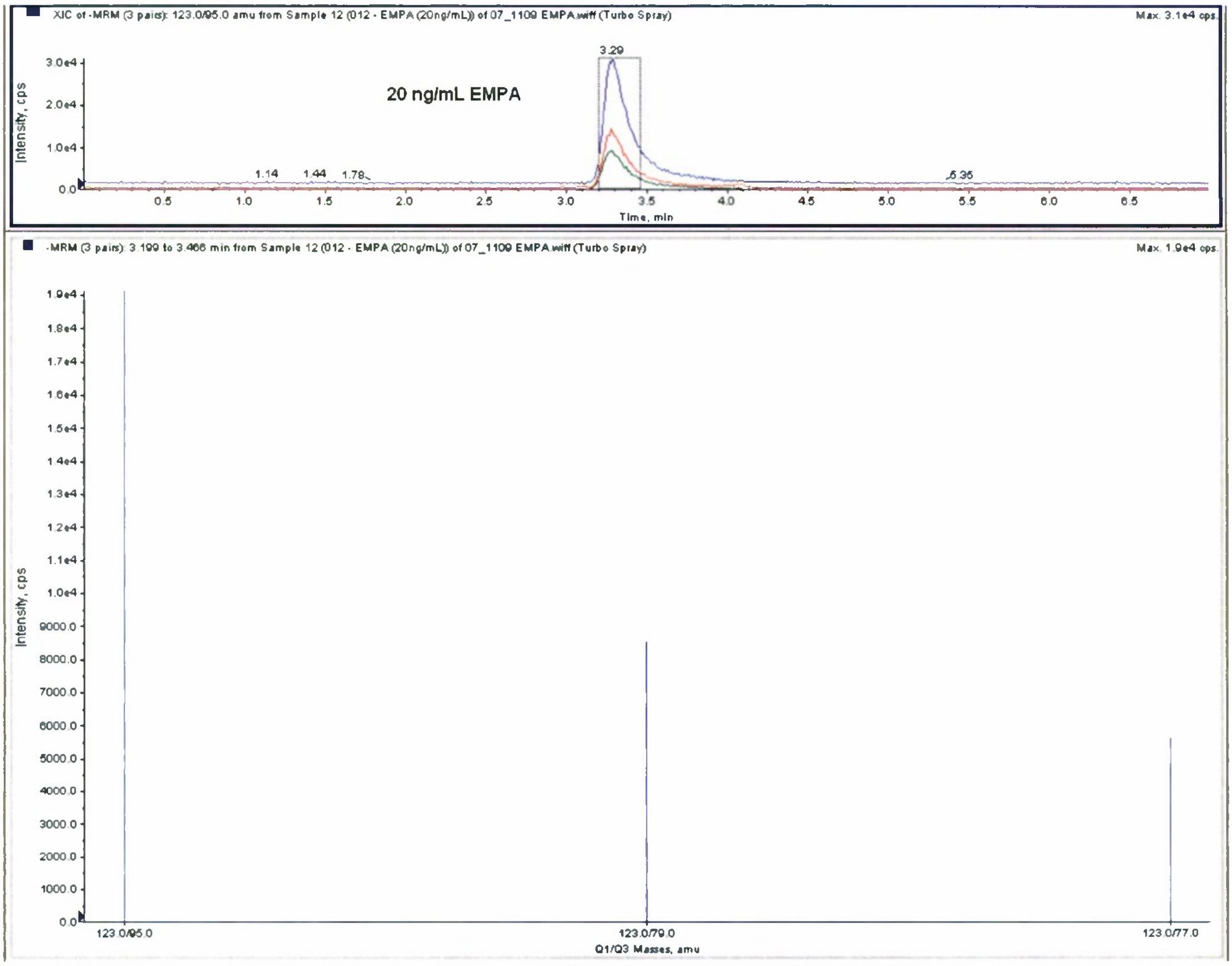
Mobile Phase
Aqueous:
95% dH2O
5% Acetonitrile
0.1% Formic Acid
5mM Ammonium Acetate

Organic:
95% Acetonitrile
5% dH2O
0.1% Formic Acid
5mM Ammonium Acetate

EMPA Chromatogram - 408-LCE DATA ANALYSIS



EMPA MS/MS Spectrum - 408-LCE DATA ANALYSIS



METHOD D: GC/MSD METHOD FOR VX (GCE VX_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of VX in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with an autosampler.

AUTHORS
Matt Shue (SAIC)
Michelle Sheahy (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
VX, O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate, CAS 50782-69-9

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent VX in liquid extraction samples. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. This method was outside the low-level scope; however, some testing may need use of higher range. Sample throughput is approximately six (6) samples per hour.

ANALYTE CONCENTRATION RANGE
This method is intended for samples containing higher quantities of VX. This method can detect VX solution concentrations from 250 to 2000 ng/mL.

This method utilizes five calibration standards at concentrations of 250, 500, 750, 1000, and 2000 ng/ml VX. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in isopropyl alcohol.

The method performance for VX is as follows:

- Quantitative Method
- Calibration range: 250 to 2000 ng/mL VX
- Calibration model: Quadratic
- Calibration weighting: none
- Limit of Detection (LOD): 32.01 ng/mL
- Limit of Quantitation (LOQ): 97.00 ng/mL
- Sample Solvent: isopropyl alcohol.
- Quant Ion: 114

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent Isopropyl alcohol (C_3H_8O; CAS #67-63-0) and containing the chemical agent VX. No significant method interferents have been identified. Users of this method should confirm that the test material and

solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute VX standards prepared in high purity isopropyl alcohol solvent. Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer

operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                          "VX_Deans.M"
                   ECBC Decon Sciences Team
                    408-GCE Method Summary

     INSTRUMENT CONTROL PARAMETERS:    GCE (6890GC - 5975MSD)
     --------------------------------------------------------

D:\GC-MS METHODS\VX_Deans.M

Control Information
------- -----------
Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes

=========================================================================
                     AGILENT DEANS SWITCH PARAMETERS
=========================================================================

METHOD: 408-GCE_Deans.M

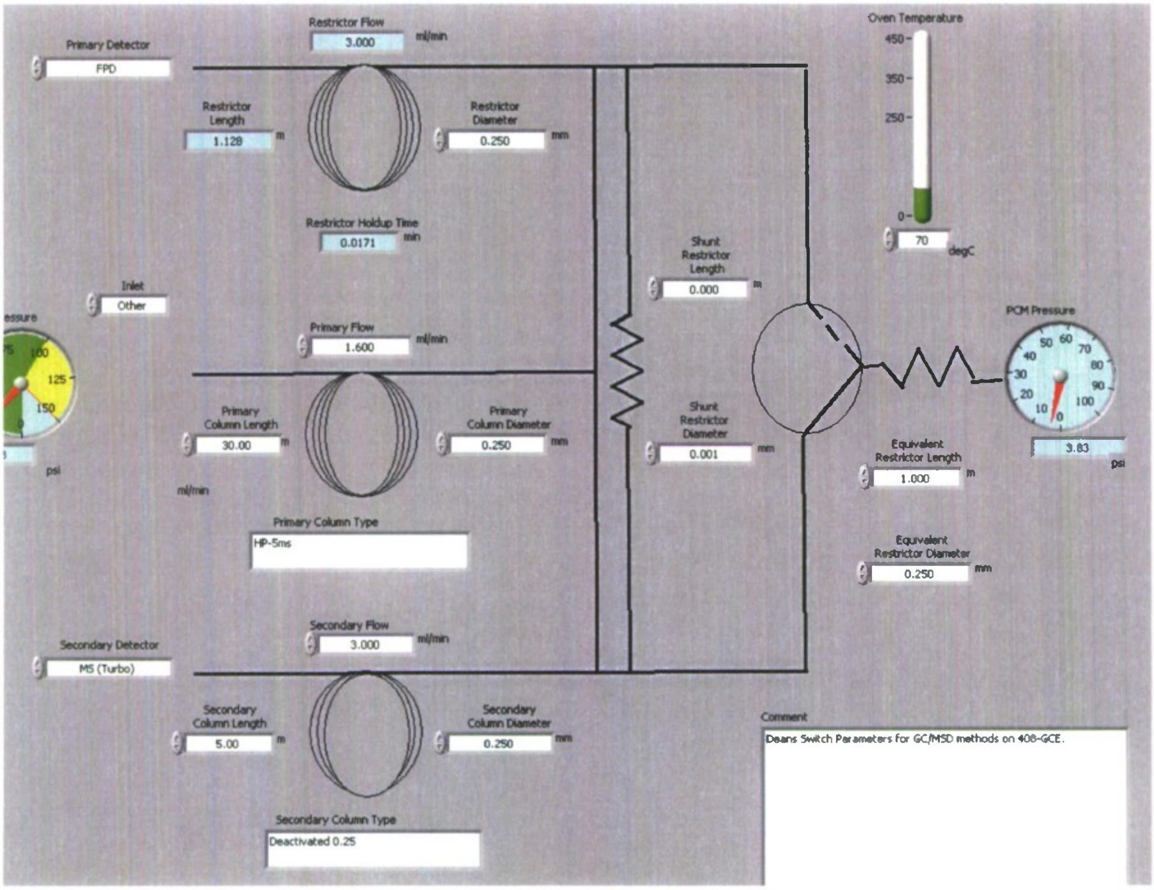
      Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.

CALCULATION RESULTS:
                                  Primary Column   Secondary Column
Inlet Pressure:                        19.53            3.83
   Avg. Linear Velocity (cm/sec):      34.72            154.76
   Hold up Time (min):                 1.44             0.054

Restrictor Length (m):                                  1.128
   Restrictor Hold Up Time (min):                       0.017

CALCULATION INPUTS
                                  Primary Column   Secondary Column
Length (m):                            30.00            5.00
i.d. (MM):                              0.25            0.25
Flow (ml/min):                          1.60            3.00
Detector:                              FPD              MS (Turbo)
Detector Pressure (abs):               14.70            0.00
Carrier Gas:                                            Helium
Pressure Units:                                         psi
Oven Temperature:                                       70.00
Restrictor Diameter:                                    0.25
Equivalent Restrictor Diameter (mm):                    0.25
Equivalent Restrictor Length (m):                       1.000
```

DEANS SWITCH CALCULATOR



==

GERSTEL CIS

==

TEMPERATURE PROGRAM
Initial Temperature : 70 'C
Equilibration Time : 0.05 min
Initial Time : 0.20 min
Ramp 1
Rate 1 : 12.0 'C/s
End Temp 1 : 280 'C
Hold Time 1 : 3.00 min
Ramp 2
Rate 2 : 0.0 'C/s

CRYO COOLING
Cryo Cooling : used

GERSTEL MPS Liquid Injection

Syringe : 10ul

```
SAMPLE PARAMETERS
Inj. Volume              : 1.0 uL
Inj. Speed               : 25.00 uL/s
Fill Volume              : 10.0 uL
Fill Strokes             : 3

Fill Speed               : 5.00 uL/s
Eject Speed              : 100.00 uL/s
Viscositiy Delay         : 1.0 s

Air Volume               : 0.0 uL
Pre Inj. Delay           : 0.00 s
Post Inj. Delay          : 0.00 s
Inj. Penetration         : 40.00 mm
Vial Penetration         : 31.00 mm

CLEANING PARAMETERS
Preclean Sample          : 0

Preclean Solv.1          : 1
Postclean Solv.1         : 3
Fill Speed Solv.1        : 5.00 uL/s
Viscosity Delay Solv.1   : 1.0 s
Eject Speed Solv.1       : 100.00 uL/s

Preclean Solv.2          : 1
Postclean Solv.2         : 3
Fill Speed Solv.2        : 5.00 uL/s
Viscosity Delay Solv.2   : 1.0 s
Eject Speed Solv.2       : 100.00 uL/s

==========================================================================
                              6890 GC METHOD
==========================================================================

OVEN
Initial temp:  100 'C (On)               Maximum temp:  325 'C
Initial time:  0.00 min                 Equilibration time:  0.25 min
Ramps:
#  Rate  Final temp  Final time
1 35.00      300        2.00
2   0.0(Off)
Post temp:  50 'C
Post time:  0.00 min
Run time:  7.71 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (CIS3)
Mode:  Split                            Mode:  Solvent Vent
Initial temp:  200 'C (Off)             Initial temp:  250 'C (Off)
Pressure:  0.00 psi (Off)               Pressure:  19.53 psi (On)
Total flow:  3.7 mL/min                 Vent time:  0.20 min
Gas saver:  Off                         Vent flow:  20.0 mL/min
Gas type:  Helium                       Vent Pressure:  19.5 psi
                                         Purge flow:  50.0 mL/min
```

Purge time: 3.00 min
Total flow: 54.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium
Initial pressure: 3.80 psi (On)

Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

AUX PRESSURE 5
Description:
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

VALVES
Valve 1 Switching Off
Description:

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
5.10	Valve 1:	On
6.10	Valve 1:	Off

GC Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number : AB001
Column 2 Inventory Number : AB002

==
5975 MS ACQUISTION PARAMETERS
==

General Information
------- -----------
Tune File : atune.u
Acquistion Mode : SIM

MS Information
-- -----------
Solvent Delay : 5.10 min

EM Absolute : False
EM Offset : 400
Resulting EM Voltage : 2400.0*

[Sim Parameters]

GROUP 1
Group ID : VX
Resolution : High
Plot 1 Ion : 72.00

Ions/Dwell In Group:

```
(Mass, Dwell)
(72.00, 50)
(114.00, 50)
(127.00, 50)
(167.00, 50)

[MSZones]

MS Quad                   : 150 C   maximum 200 C
MS Source                 : 230 C   maximum 250 C

END OF MS ACQUISITION PARAMETERS
```

TUNE PARAMETERS*

MSD Specific Values automatically determined and set when performing an Autotune.

```
END OF TUNE PARAMETERS
------------------------------------

END OF INSTRUMENT CONTROL PARAMETERS
------------------------------------
```

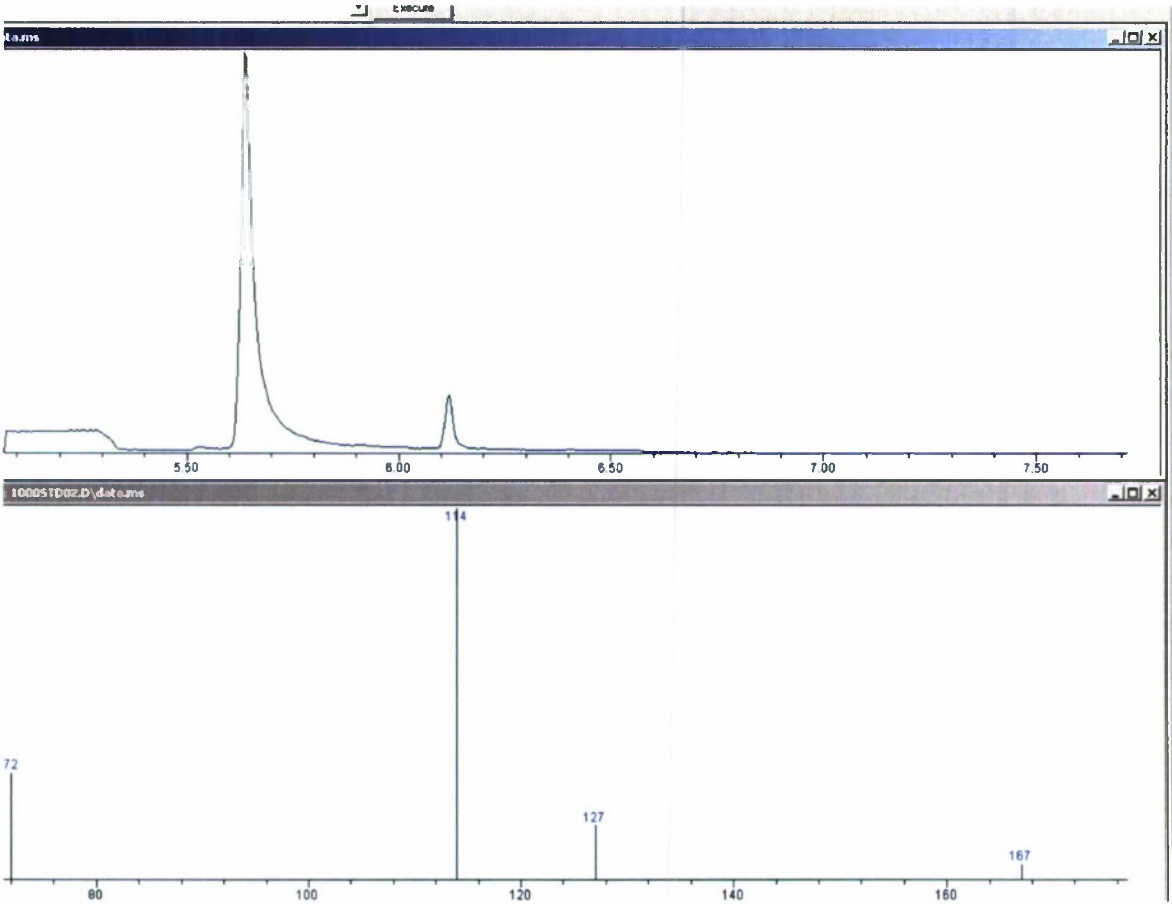
VX SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: VX   Formula: $C_{11}H_{26}NO_2PS$ MW: 267
CAS#: 50782-69-9 NIST#: 226161 ID#: 68951 DB: mainlib

A sample spectrum from this program is provided.

VX TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



Approximate Method retention time for VX: 5.64 minutes.

METHOD E: GC-MS METHOD FOR LOW-LEVEL VX VAPOR SAMPLE ANALYSIS (GCV VX-DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of VX as the G-Analog in vapor samples for chemical agent decontamination testing using a GC/MSD with a thermal desorption unit.

AUTHORS
Morgan Hall (SAIC)
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
VX, O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate, CAS 50782-69-9.

G-Analog, Ethyl methylphosphonofluoridate, CAS 673-97-2

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent VX as Ethyl methylphosphonofluoridate (G-analog) in vapor samples. This method is based on the collection of vapor samples on tubes containing solid sorbent material following chemical agent decontamination performance evaluation testing. The method is optimized for the detection requirements for the analysis of a 2-inch diameter test surface area. It is anticipated that this method can support larger item vapor testing. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to detect and quantify the chemical agent VX as Ethyl methylphosphonofluoridate (G-analog) in vapor samples This method can detect VX as the G-Analog with a mass on column range of 3.0 to 500 ng. Sample collection parameters are adjusted to collect vapor samples in this mass range.

This method utilizes seven calibration standards at concentrations of 3, 10, 25, 50, 100, 250, and 500 ng VX. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in isopropyl alcohol.

The method performance for VX as G-analog is as follows:

- Quantitative Method
- Calibration range: 3 to 500 ng VX on column
- Calibration model: linear with intercept
- Calibration weighting: 1 over the mass squared
- Limit of Detection (LOD): 0.86 ng

- Limit of Quantitation (LOQ): 2.62 ng
- Spiking sample Solvent: isopropyl alcohol
- Quant Ion: 99

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for vapor samples containing the chemical agent VX as the G-Analog. No significant method interferents have been identified. Users of this method should confirm that the test material does not offgas an interferent in the detection region of interest.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The vapor samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction of a vapor sample is performed using a MARKES Thermal Desorption System (TDS). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and MARKES. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute VX standards prepared in high purity isopropyl alcohol solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

The mass of agent on tube should be estimated for vapor samples to minimize saturation of the detector.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, tube spiking, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as mass on tube (ng). Mass on tube can be calculated in the instrument control software (e.g., Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported mass is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"VX_Deans.M"
ECBC Decon Sciences Team
408-GCV Method Summary

NOTE: VX is analyzed as the G-analog.

INSTRUMENT CONTROL PARAMETERS: GCV (6890GC - 5975MSD)

D:\GC-MS METHODS\VX-DEANS.M

Control Information

Sample Inlet	GC
Injection Source	Manual
Injection Location	Front
Mass Spectrometer	Enabled

AGILENT DEANS SWITCH PARAMETERS

METHOD: 408-GCV_Deans.M

Comment: Deans Switch Parameters for 408-GCV w/ Markes Thermal Desorption System.

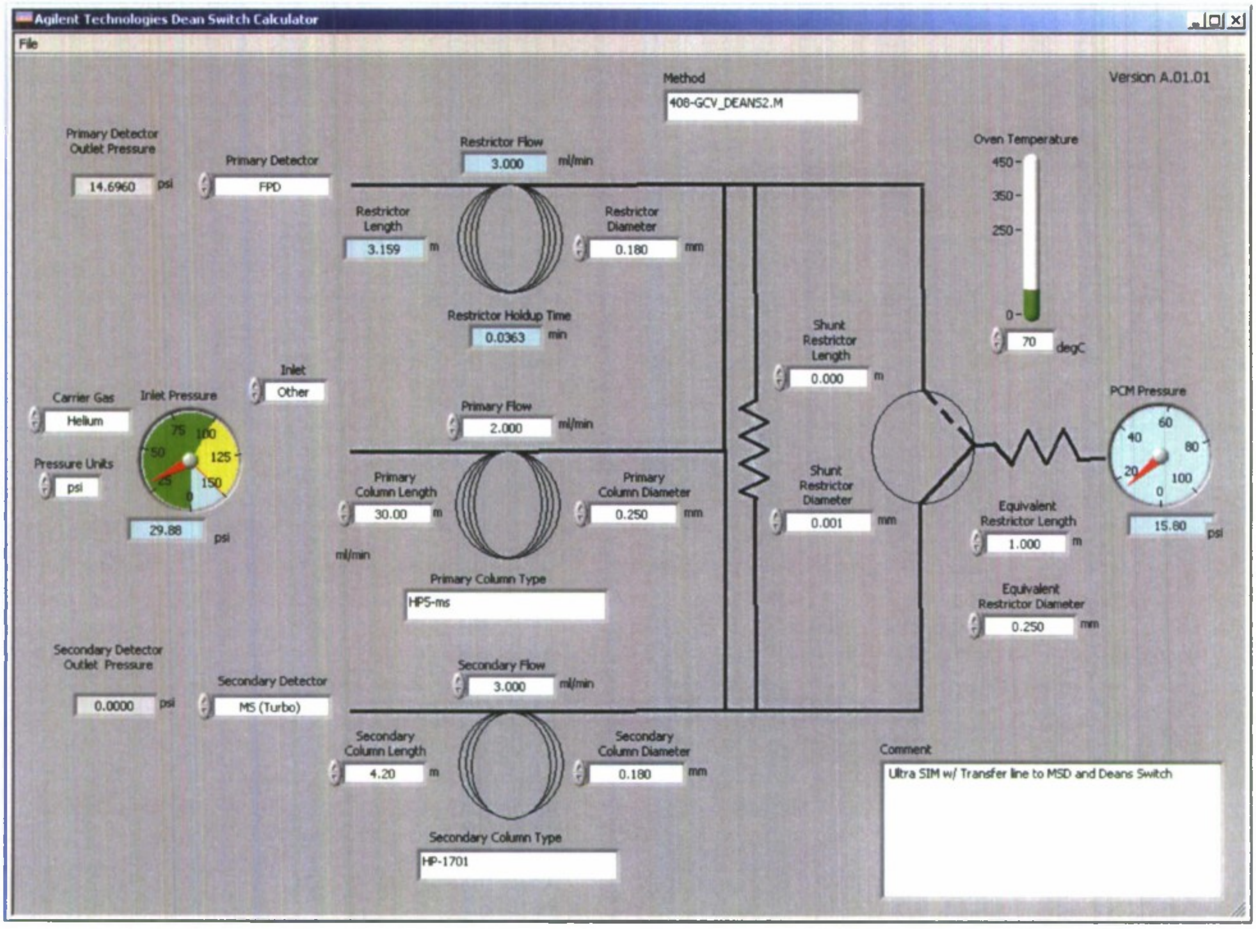
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	29.88	15.80
Avg. Linear Velocity (cm/sec):	30.58	168.85
Hold up Time (min):	1.64	0.041
Restrictor Length (m):		3.159
Restrictor Hold Up Time (min):		0.036

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	4.20
i.d. (MM):	0.25	0.25
Flow (ml/min):	2.00	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70
Restrictor Diameter:		0.18
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR

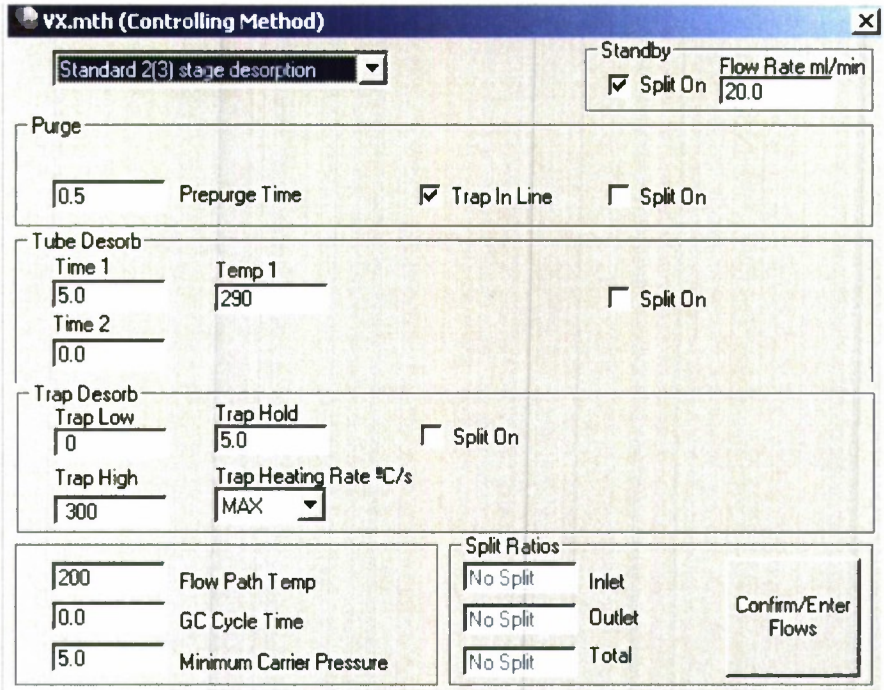



```
===========================================================================
                          MARKES TDS UNITY METHOD
===========================================================================

UNITY Method = VX.mth

Operating Mod = Standards Two Stage
Standby Flow = 20
Purge Time = 0.2
Minimum Carrier Pressure = 5
Purge Flow = 40
Ola Split Flow = 20
Oven Temperature 1 = 290
Desorb Time 1 = 5
Desorb Time 2 = 0
Desorb Tube Split = FALSE
Desorb Tube Flow = 20
Dry Purge Time = 1
Standard Injection Time = 0
Trap Low = 10
Trap High = 300
Trap Hold = 5
Trap Split = False
Trap Heat Rate = 0
Desorb Flow = 40
```

```
Tube Desorb Split = 40
Trap Desorb Split = 20
Inlet Split Ratio = No Split
Outlet Split Ration = No Split
Total Split Ratio = No Split
Flow Path Temperature = 200
GC Cycle Time = 0
```




```
=========================================================================
                              6890 GC METHOD
=========================================================================

OVEN
   Initial temp:  70 'C (On)               Maximum temp:  300 'C
   Initial time:  0.00 min                 Equilibration time:  0.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1 50.00   290        0.60
      2   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  5.00 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  250 'C (On)
   Pressure:  29.88 psi (On)
   Purge flow:  49.9 mL/min
   Purge time:  999.99 min
   Total flow:  55.5 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                COLUMN 2
```

```
   Capillary Column                               (not installed)
   Model Number:  Agilent 19091S-433
   HP-5MS  5% Phenyl Methyl Siloxane
   Max temperature:  325 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant pressure
   Pressure:  29.88 psi
   Nominal initial flow:  3.2 mL/min
   Average velocity:  58 cm/sec
   Inlet:  Front Inlet
   Outlet:  Other
   Outlet pressure:  ambient

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
   Temperature:  250 'C (On)
   Hydrogen flow:  75.0 mL/min (On)
   Oxidizer flow:  100.0 mL/min (On)
   Oxidizer Gas Type: Air
   Mode:  Constant makeup flow
   Makeup flow:  25.0 mL/min (On)
   Makeup Gas Type: Helium
   Flame:  On
   Lit offset:  2.00
   Photo multiplier:  On

SIGNAL 1
   Data rate:  20 Hz
   Type:  back detector
   Save Data:  On
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

SIGNAL 2
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

COLUMN COMP 1
   (No Detectors Installed)

COLUMN COMP 2
   (No Detectors Installed)

THERMAL AUX 1
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

THERMAL AUX 2
   Unknown Thermal Aux Type

AUX PRESSURE 3
   Description: Deans Switch
   Gas Type:  Helium
   Initial pressure:  15.80 psi (On)
   Initial time:  0.00 min
      #  Rate  Final pres  Final time
      1   0.0(Off)

AUX PRESSURE 4
   Description:
   Gas Type:  Helium
   Initial pressure:  17.60 psi (Off)

AUX PRESSURE 5
   Description:
```

```
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)

VALVES                                       POST RUN
   Valve 1  Switching Off                       Post Time: 0.00 min
      Description:

TIME TABLE
   Time       Specifier                          Parameter & Setpoint
      2.30       Valve 1:                           On
      2.60       Valve 1:                           Off
```

GC Injector

```
     Front Injector:
No parameters specified

     Back Injector:
No parameters specified

 Column 1 Inventory Number : AB002
 Column 2 Inventory Number :
```

MS ACQUISITION PARAMETERS

```
General Information
------- -----------
Tune File                 : atune.u
Acquistion Mode           : SIM

MS Information
-- -----------
Solvent Delay             : 2.20 min

EM Absolute               : False
EM Offset                 : 200
Resulting EM Voltage      : 2247.1*

[Sim Parameters]

GROUP 1
Group ID                  : VX
Resolution                : High
Plot 1 Ion                : 111.00
Ions/Dwell In Group

(Mass, Dwell)
(81.00, 75)
(99.00, 75)
(111.00, 75)
(125.00, 75)

[MSZones]

MS Quad                   : 150 C   maximum 200 C
MS Source                 : 230 C   maximum 250 C
Timed Events
```

----- ------

[Timed MS Detector Entries]

Time (min)	State (MS on/off)
2.30	On
2.60	Off

TUNE PARAMETERS*
----

*MSD Specific Values automatically determined and set when performing an Autotune.

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

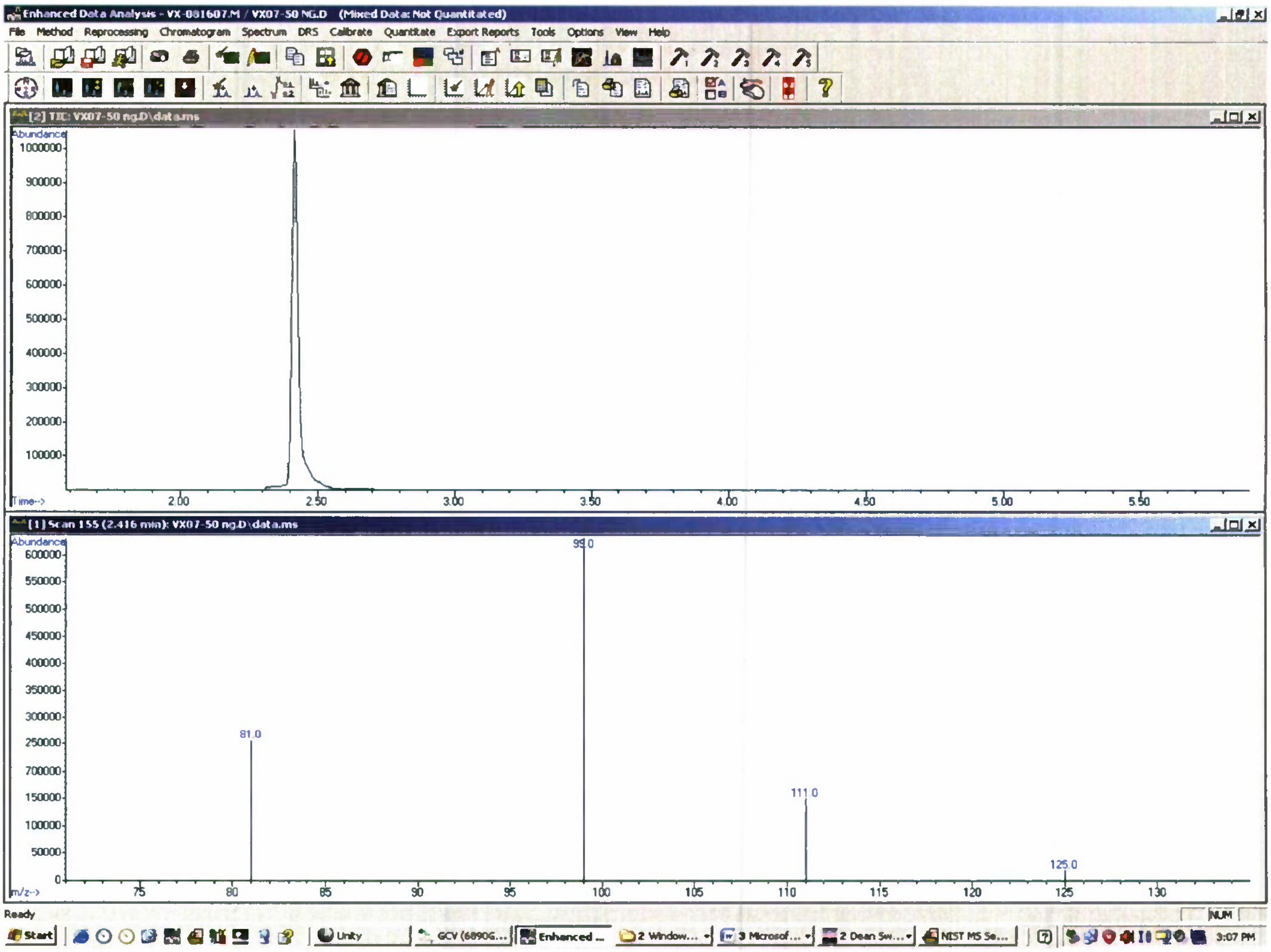
G-ANALOG SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Ethyl methylphosphonofluoridate (G-Analog) Formula: $C_3H_8FO_2P$
MW: 126 CAS#: 673-97-2 NIST#: 226118 ID#: 56237 DB: mainlib

A sample spectrum from this program is provided.

G-ANALOG SPECTRUM (SIM) - 408-GCV DATA ANALYSIS



Approximate Method Retention Time for G-Analog: 2.416 minutes.

METHOD F: GC-MS METHOD FOR LOW-LEVEL HD VAPOR SAMPLE ANALYSIS (GCV HDLL-DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of HD in vapor samples for chemical agent decontamination testing using a GC/MSD with a thermal desorption unit.

AUTHORS
Morgan Hall (SAIC)
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
Mustard, HD, Bis(2-chloroethyl)sulfide CAS 505-60-2

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent HD in vapor samples. This method is based on the collection of vapor samples on tubes containing solid sorbent material following chemical agent decontamination performance evaluation testing. The method is optimized for the detection requirements for the analysis of a 2-inch diameter test surface area. It is anticipated that this method can support larger item vapor testing. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This HD low level method can detect HD with a mass on column range of 0.1 to 500 ng. Sample collection parameters are adjusted to collect vapor samples in this mass range. No sample split on the Markes unit is needed.

This method utilizes five calibration standards at concentrations of 0.1, 1, 10, 100, and 500 ng HD. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in chloroform.

The method performance for HD is as follows:

- Quantitative Method
- Calibration range: 0.1 to 500 ng HD on column.
- Calibration model: linear forced zero calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 0.47 ng
- Limit of Quantitation (LOQ): 1.42 ng
- Spiking sample Solvent: chloroform.
- Quant Ion: 111

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for vapor samples containing the chemical agent HD. No significant method interferents have been identified. Users of this method should confirm that the test material does not offgas an interferent in the detection region of interest.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The vapor samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction of a vapor sample is performed using a MARKES Thermal Desorption System (TDS). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and MARKES. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute HD standards prepared in high purity hexane or chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

The mass of agent on tube should be estimated for vapor samples to minimize saturation of the detector.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, tube spiking, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as mass on tube (ng). Mass on tube can be calculated in the instrument control software (e.g., Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported mass is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"HDLL-Deans.M"
ECBC Decon Sciences Team
408-GCV Method Summary

INSTRUMENT CONTROL PARAMETERS: GCV (6890GC - 5975MSD)

D:\GC-MS METHODS\HDLL-DEANS.M

Control Information

Sample Inlet	: GC
Injection Source	: Manual
Injection Location	: Front
Mass Spectrometer	: Enabled

AGILENT DEANS SWITCH PARAMETERS

METHOD: 408-GCV_Deans.M

Comment: Deans Switch Parameters for 408-GCV w/ Markes Thermal Desorption System.

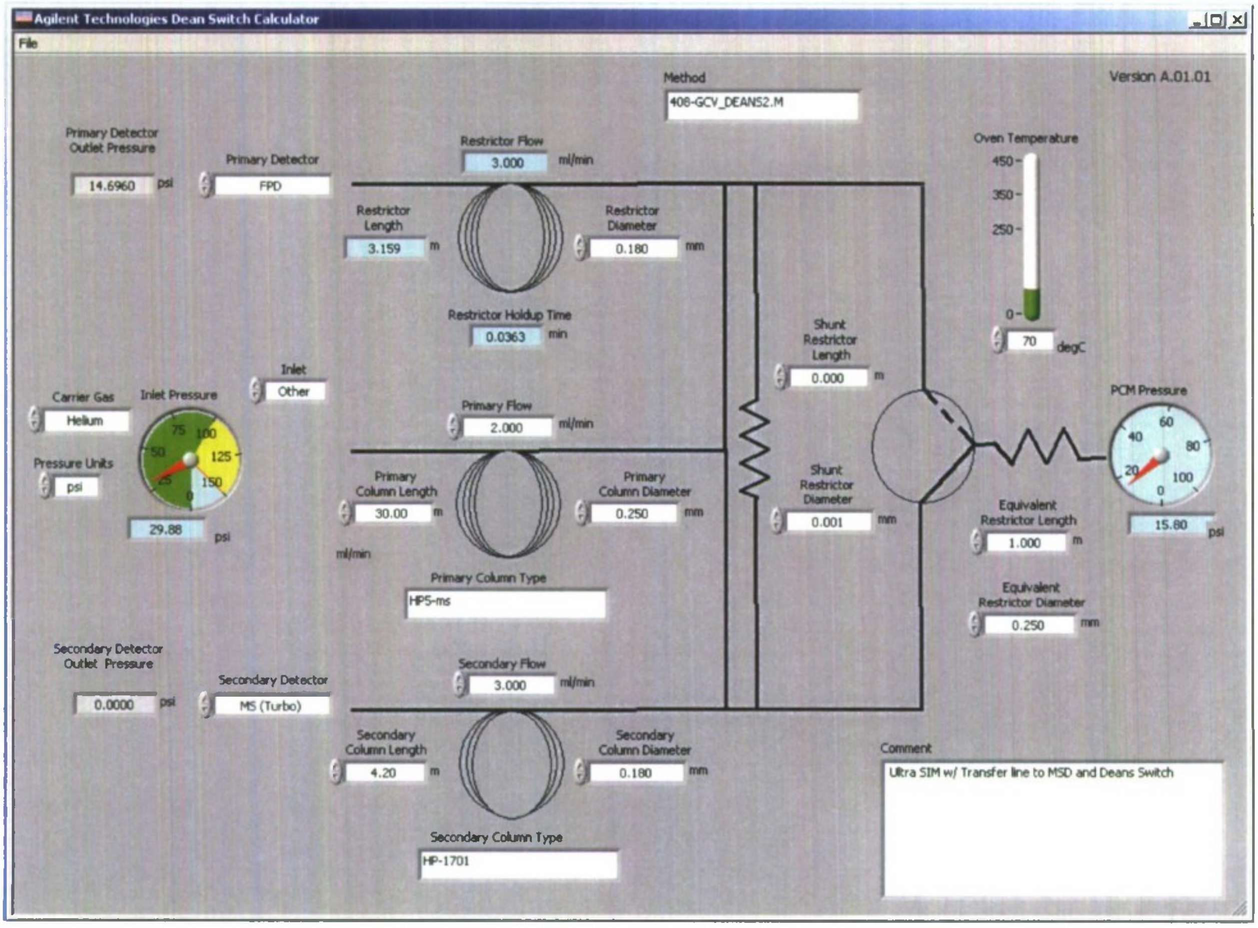
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	29.88	15.80
Avg. Linear Velocity (cm/sec):	30.58	168.85
Hold up Time (min):	1.64	0.041
Restrictor Length (m):		3.159
Restrictor Hold Up Time (min):		0.036

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	4.20
i.d. (MM):	0.25	0.25
Flow (ml/min):	2.00	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70
Restrictor Diameter:		0.18
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

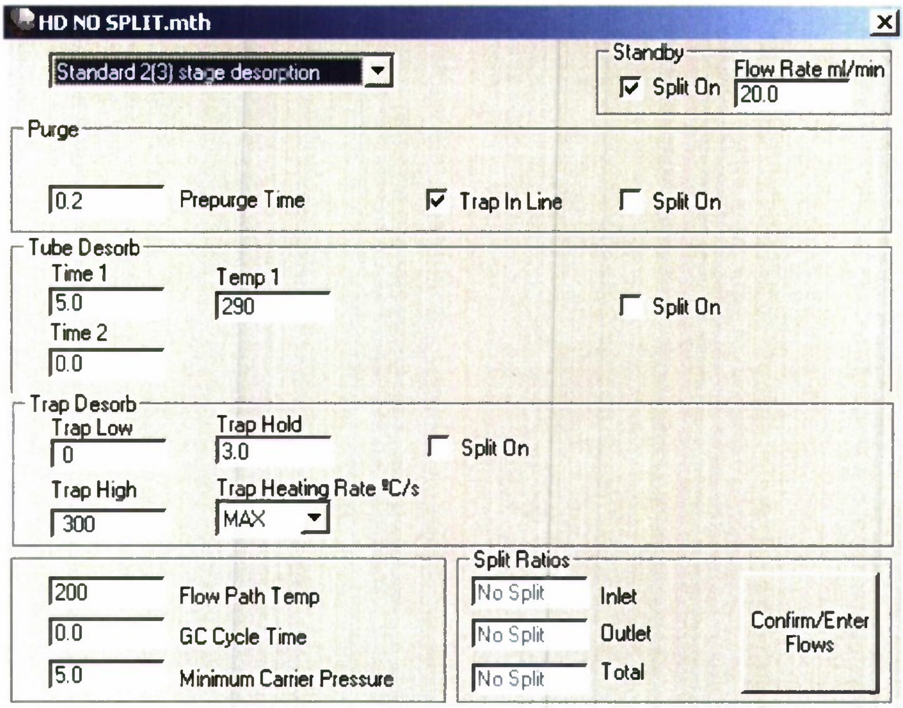
DEANS SWITCH CALCULATOR




```
========================================================================
                          MARKES TDS UNITY METHOD
========================================================================
UNITY Method = HDLL.mth

Operating Mod = Standards Two Stage
Standby Flow = 20
Purge Time = 0.2
Minimum Carrier Pressure = 5
Purge Trap in Line = TRUE
Purge Flow = 20
Oven Temperature 1 = 290
Desorb Time 1 = 5
Desorb Time 2 = 0
Desorb Tube Split = FALSE
Desorb Tube Flow = 20
Dry Purge Time = 1
Standard Injection Time = 1
Trap Low = 0
Trap High = 300
Trap Hold = 5
Column Flow = 0
Desorb Flow = 0
Tube Desorb Split = 0
Trap Desorb Split = 0
Inlet Split Ratio = No Split
```

```
Outlet Split Ration = No Split
Total Split Ratio = No Split
Flow Path Temperature = 200
GC Cycle Time = 0
```




```
=========================================================================
                              6890 GC METHOD
=========================================================================

OVEN
   Initial temp:  70 'C (On)                Maximum temp:  300 'C
   Initial time:  0.00 min                  Equilibration time:  0.00 min
   Ramps:
      # Rate Final temp Final time
      1 30.00      220        0.50
      2 0.0(Off)
   Post temp:  70 'C
   Post time:  0.00 min
   Run time:  5.50 min

FRONT INLET (SPLIT/SPLITLESS)            BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  250 'C (On)
   Pressure:  29.88 psi (On)
   Purge flow:  49.9 mL/min
   Purge time:  999.99 min
   Total flow:  55.5 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                 COLUMN 2
   Capillary Column                         (not installed)
   Model Number:  Agilent 19091S-433
```

HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 29.88 psi
Nominal initial flow: 3.2 mL/min
Average velocity: 58 cm/sec
Inlet: Front Inlet
Outlet: Other
Outlet pressure: ambient

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description:
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: Deans Switch
Gas Type: Helium
Initial pressure: 15.80 psi (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

AUX PRESSURE 4
Description:
Gas Type: Helium
Initial pressure: 17.60 psi (Off)

AUX PRESSURE 5
Description:
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

```
VALVES                                  POST RUN
   Valve 1  Switching Off                  Post Time: 0.00 min
      Description:

TIME TABLE
   Time        Specifier                       Parameter & Setpoint
      4.20        Valve 1:                        On
      4.60        Valve 1:                        Off
                                 GC Injector


     Front Injector:
No parameters specified

     Back Injector:
No parameters specified

 Column 1 Inventory Number : AB002
 Column 2 Inventory Number :


                                  MS ACQUISITION PARAMETERS
General Information
------- -----------
Tune File                : atune.u
Acquistion Mode          : SIM


MS Information
-- -----------

Solvent Delay            : 1.00 min

EM Absolute              : False
EM Offset                : 200
Resulting EM Voltage     : 2247.1*

[Sim Parameters]

GROUP 1
Group ID                 : HD
Resolution               : High
Plot 1 Ion               : 109.00
Ions/Dwell In Group
(Mass,  Dwell)
(109.00, 75)
(111.00, 75)
(158.00, 75)
(160.00, 75)

[MSZones]

MS Quad                  : 150 C   maximum 200 C
MS Source                : 230 C   maximum 250 C

Timed Events
```

```
----- ------

[Timed MS Detector Entries]

Time (min)          State (MS on/off)
4.20                     On
4.60                     Off
```

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS*
----

*MSD Specific Values automatically determined and set when performing an Autotune.

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

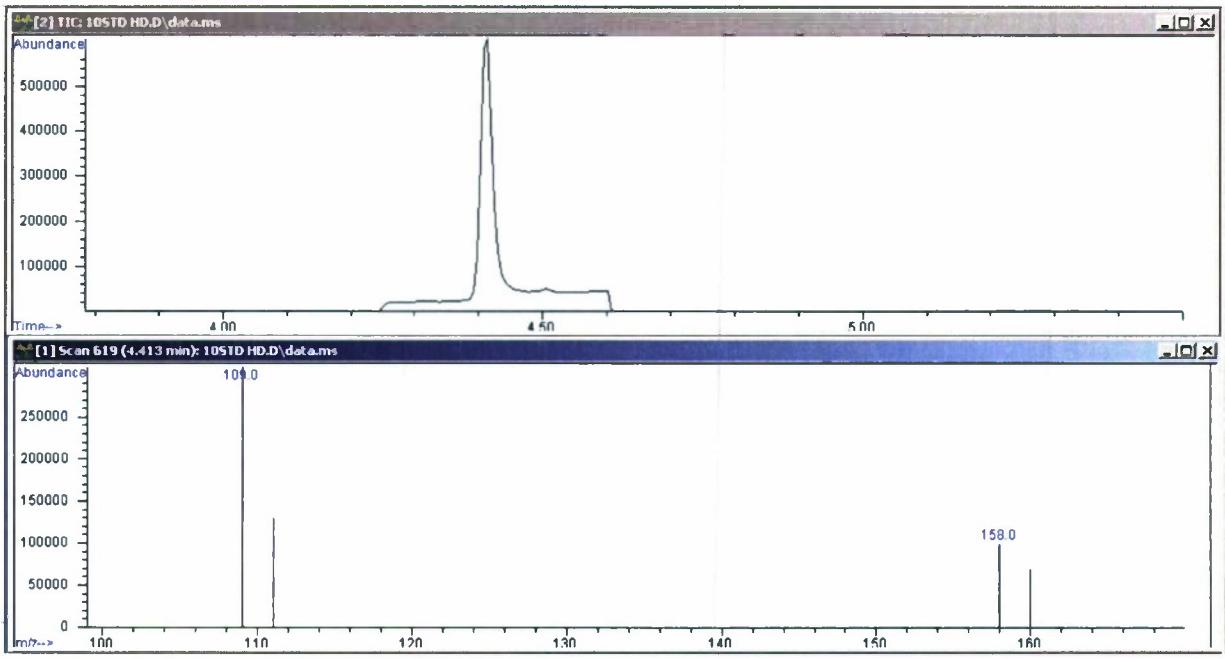
HD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Mustard Gas Formula: $C_4H_8Cl_2S$ MW: 158
CAS#: 505-60-2 NIST#: 289463 ID#: 65664 DB: mainlib

A sample spectrum from this program is provided.

HD SPECTRUM (SIM) - 408-GCV DATA ANALYSIS



Approximate Method retention time for HD: 4.408 minutes.

METHOD G: GC-MS METHOD FOR HIGH-LEVEL HD VAPOR SAMPLE ANALYSIS (GCV HDHL-DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of HD in vapor samples for chemical agent decontamination testing using a GC/MSD with a thermal desorption unit.

AUTHORS
Morgan Hall (SAIC)
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
Mustard, HD, Bis(2-chloroethyl)sulfide CAS 505-60-2

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent HD in vapor samples. This method is based on the collection of vapor samples on tubes containing solid sorbent material following chemical agent decontamination performance evaluation testing. The method is optimized for the detection requirements for the analysis of a 2-inch diameter test surface area. It is anticipated that this method can support larger item vapor testing. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This method is a complementary method to the low-level method for the analysis of higher concentrations of HD from vapor sorbent tube samples. This method can detect HD concentrations from 100 to 2000 ng. Sample collection parameters are adjusted to collect vapor samples in this mass range. With this high level method a 95 mL/min sample split is needed with the Markes system in order to achieve these higher masses. No parameter changes are needed with the Agilent GC/MSD system.

This method utilizes five calibration standards at concentrations of 100, 500, 1000, 1500, and 2000 ng HD. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in chloroform.

The method performance for HD is as follows:

- Quantitative Method
- Calibration range: 100 to 2000 ng HD on column.
- Calibration model: linear with intercept
- Calibration weighting: 1 over mass squared
- Limit of Detection (LOD): 39.20 ng
- Limit of Quantitation (LOQ): 118.79 ng
- Spiking sample Solvent: chloroform

- Quant Ion: 111

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for vapor samples containing the chemical agent HD. No significant method interferents have been identified. Users of this method should confirm that the test material does not offgas an interferent in the detection region of interest.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The vapor samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction of a vapor sample is performed using a MARKES Thermal Desorption System (TDS). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and MARKES. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute HD standards prepared in high purity hexane or chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined,

PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

The mass of agent on tube should be estimated for vapor samples to minimize saturation of the detector.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, tube spiking, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as mass on tube (ng). Mass on tube can be calculated in the instrument control software (e.g., Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported mass is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"HDHL-Deans.M"
ECBC Decon Sciences Team
408-GCV Method Summary

INSTRUMENT CONTROL PARAMETERS: GCV (6890GC - 5975MSD)

D:\GC-MS METHODS\HDHL-DEANS.M

Control Information

Sample Inlet	GC
Injection Source	Manual
Injection Location	Front
Mass Spectrometer	Enabled

AGILENT DEANS SWITCH PARAMETERS

METHOD: 408-GCV_Deans.M

Comment: Deans Switch Parameters for 408-GCV w/ Markes Thermal Desorption System.

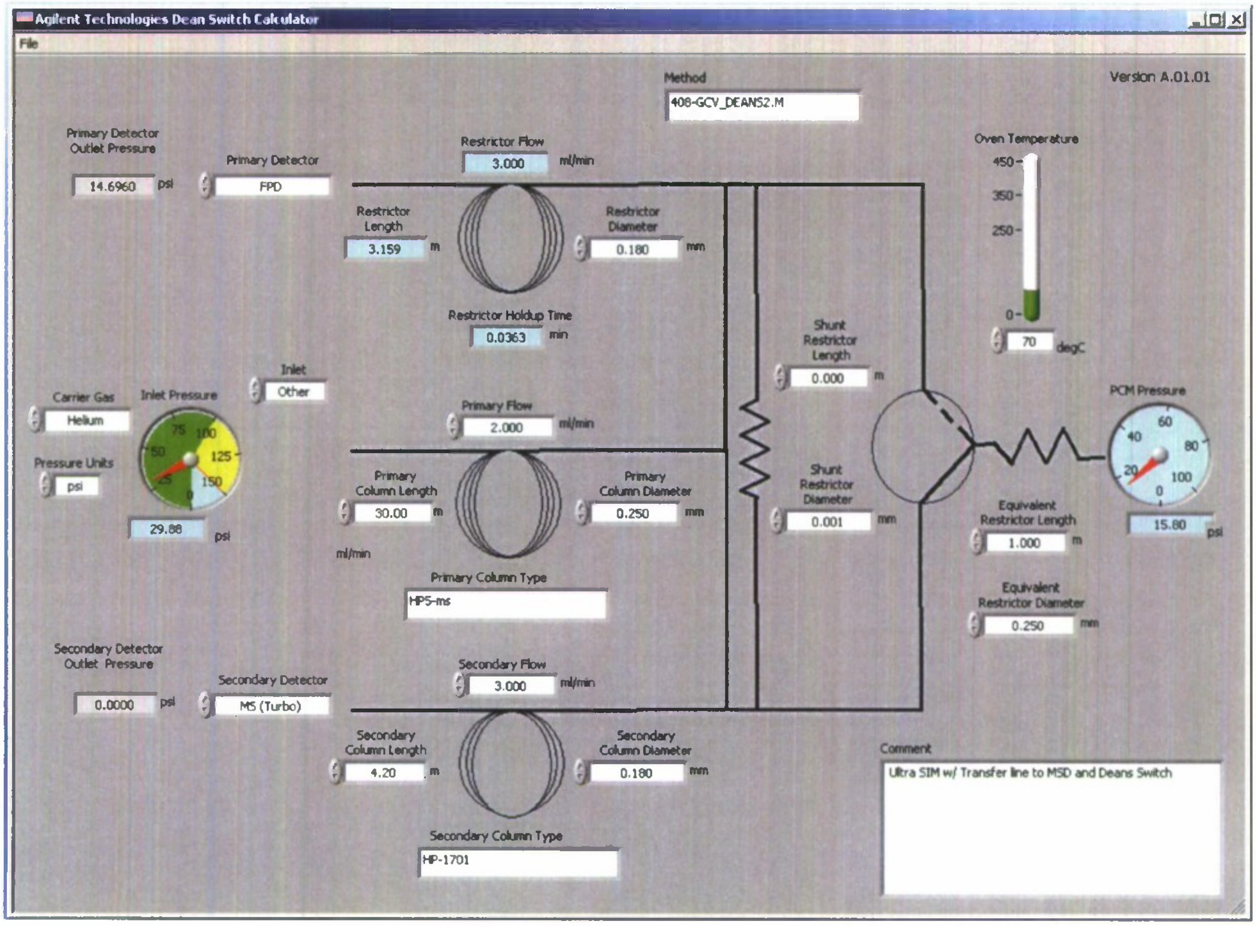
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	29.88	15.80
Avg. Linear Velocity (cm/sec):	30.58	168.85
Hold up Time (min):	1.64	0.041
Restrictor Length (m):		3.159
Restrictor Hold Up Time (min):		0.036

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	4.20
i.d. (MM):	0.25	0.25
Flow (ml/min):	2.00	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70
Restrictor Diameter:		0.18
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

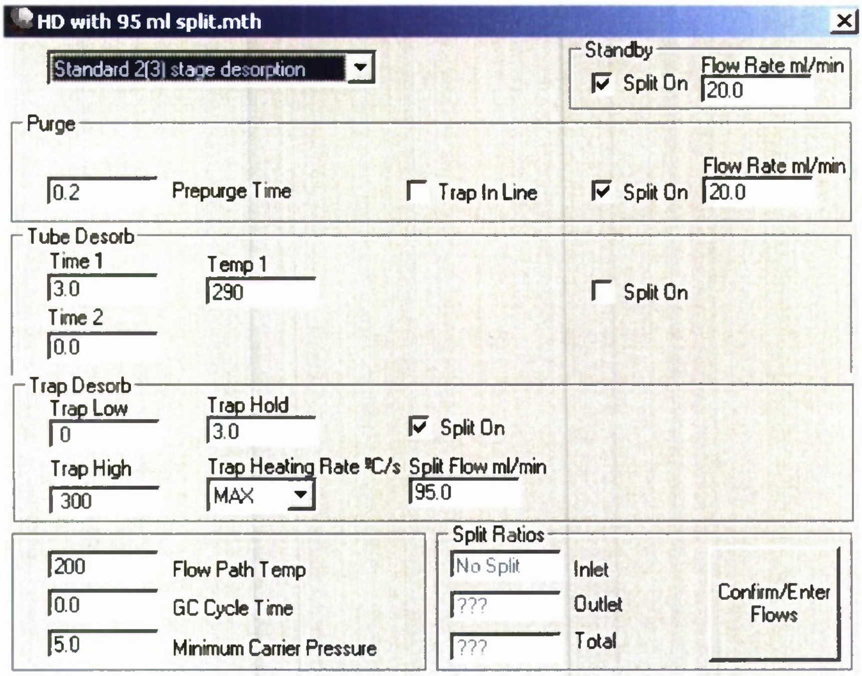
DEANS SWITCH CALCULATOR




```
=========================================================================
                           MARKES TDS UNITY METHOD
=========================================================================
UNITY Method = HDHL.mth

Operating Mod = Standards Two Stage
Standby Flow = 20
Purge Time = 0.2
Minimum Carrier Pressure = 5
Purge Trap in Line = TRUE
Purge Flow = 20
Oven Temperature 1 = 290
Desorb Time 1 = 5
Desorb Time 2 = 0
Desorb Tube Split = FALSE
Desorb Tube Flow = 20
Dry Purge Time = 1
Standard Injection Time = 1
Trap Low = 0
Trap High = 300
Trap Hold = 5
Column Flow = 0
Desorb Flow = 0
Tube Desorb Split = 0
Trap Desorb Split = 95ml/min
```

Inlet Split Ratio = No Split
Outlet Split Ration = No Split
Total Split Ratio = No Split
Flow Path Temperature = 200
GC Cycle Time = 0



==

6890 GC METHOD

==

OVEN
Initial temp: 70 'C (On)
Initial time: 0.00 min
Maximum temp: 300 'C
Equilibration time: 0.00 min
Ramps:

#	Rate	Final temp	Final time
1	30.00	220	0.50
2	0.0(Off)		

Post temp: 70 'C
Post time: 0.00 min
Run time: 5.50 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Splitless
Initial temp: 250 'C (On)
Pressure: 29.88 psi (On)
Purge flow: 49.9 mL/min
Purge time: 999.99 min
Total flow: 55.5 mL/min
Gas saver: Off
Gas type: Helium

BACK INLET (UNKNOWN)

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane

COLUMN 2
(not installed)

```
   Max temperature:  325 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant pressure
   Pressure:  29.88 psi
   Nominal initial flow:  3.2 mL/min
   Average velocity:  58 cm/sec
   Inlet:  Front Inlet
   Outlet:  Other
   Outlet pressure:  ambient

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
   Temperature:  250 'C (On)
   Hydrogen flow:  75.0 mL/min (On)
   Oxidizer flow:  100.0 mL/min (On)
   Oxidizer Gas Type: Air
   Mode:  Constant makeup flow
   Makeup flow:  25.0 mL/min (On)
   Makeup Gas Type: Helium
   Flame:  On
   Lit offset:  2.00
   Photo multiplier:  On

SIGNAL 1
   Data rate:  20 Hz
   Type:  back detector
   Save Data:  On
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

SIGNAL 2
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

COLUMN COMP 1
   (No Detectors Installed)

COLUMN COMP 2
   (No Detectors Installed)

THERMAL AUX 1
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      # Rate Final temp Final time
      1   0.0(Off)

THERMAL AUX 2
   Unknown Thermal Aux Type

AUX PRESSURE 3
   Description: Deans Switch
   Gas Type:  Helium
   Initial pressure:  15.80 psi (On)
   Initial time:  0.00 min
      # Rate Final temp Final time
      1   0.0(Off)

AUX PRESSURE 4
   Description:
   Gas Type:  Helium
   Initial pressure:  17.60 psi (Off)

AUX PRESSURE 5
   Description:
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)
```

```
VALVES                                  POST RUN
   Valve 1  Switching Off                  Post Time: 0.00 min
      Description:

TIME TABLE
   Time       Specifier                        Parameter & Setpoint
      4.20       Valve 1:                         On
      4.60       Valve 1:                         Off
                               GC Injector


     Front Injector:
No parameters specified

     Back Injector:
No parameters specified

 Column 1 Inventory Number : AB002
 Column 2 Inventory Number :


                                MS ACQUISITION PARAMETERS
General Information
------- -----------
Tune File                : atune.u
Acquistion Mode          : SIM


MS Information
-- -----------
Solvent Delay            : 1.00 min

EM Absolute              : False
EM Offset                : 200
Resulting EM Voltage     : 2247.1*

[Sim Parameters]

GROUP 1
Group ID                 : HD
Resolution               : High
Plot 1 Ion               : 109.00
Ions/Dwell In Group
(Mass,  Dwell)
(109.00, 75)
(111.00, 75)
(158.00, 75)
(160.00, 75)

[MSZones]

MS Quad                  : 150 C   maximum 200 C
MS Source                : 230 C   maximum 250 C
Timed Events
----- ------

[Timed MS Detector Entries]
```

Time (min)	State (MS on/off)
4.20	On
4.60	Off

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS*
----

*MSD Specific Values automatically determined and set when performing an Autotune.

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETER

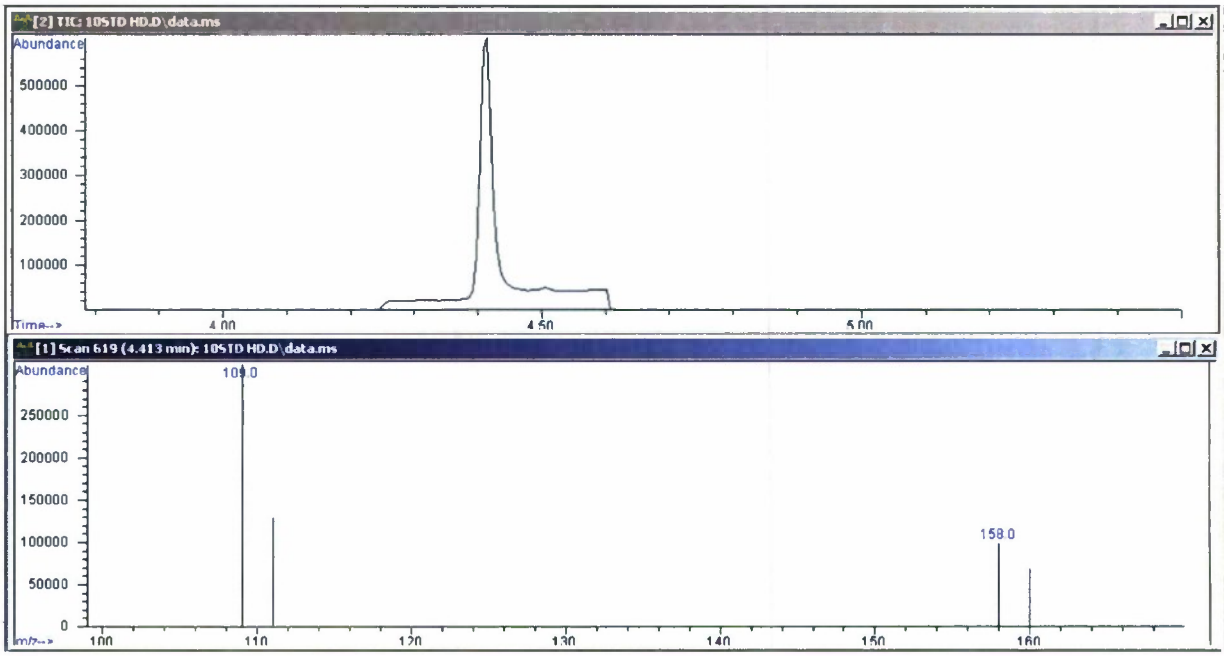
HD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Mustard Gas Formula: $C_4H_8Cl_2S$ MW: 158
CAS#: 505-60-2 NIST#: 289463 ID#: 65664 DB: mainlib

A sample spectrum from this program is provided.

HD SPECTRUM (SIM) - 408-GCV DATA ANALYSIS



Approximate Method retention time for HD: 4.408 minutes.

METHOD H: GC-MS METHOD FOR LOW-LEVEL GD VAPOR SAMPLE ANALYSIS (GCV GDLL-DEANS.M)

ANALYTICAL METHOD

TITLE

Detection of GD in vapor samples for chemical agent decontamination testing using a GC/MSD with a thermal desorption unit.

AUTHORS

Morgan Hall (SAIC)
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS

Soman, GD, O-Pinacolyl methylphosphonofluoridate; CAS 96-64-0

REVISION HISTORY

This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS

The purpose of this method is to detect and quantify the chemical agent GD in vapor samples. This method is based on the collection of vapor samples on tubes containing solid sorbent material following chemical agent decontamination performance evaluation testing. The method is optimized for the detection requirements for the analysis of a 2-inch diameter test surface area. It is anticipated that this method can support larger item vapor testing. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE

This method is for the analysis of vapor sorbent tube samples for low-level GD. This GD low level method can detect GD with a mass on column range of 0.5 to 10 ng. Sample collection parameters are adjusted to collect vapor samples in this mass range. No sample split on the Markes unit is needed.

This method utilizes five calibration standards at concentrations of 0.5, 1, 3, 5, and 10 ng GD. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in acetonitrile.

The method performance for GD is as follows:

- Quantitative Method
- Calibration range: 0.5 to 10 ng GD on column.
- Calibration model: linear forced zero calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 0.01 ng
- Limit of Quantitation (LOQ): 0.02 ng
- Spiking sample Solvent: acetonitrile
- Quant Ion: 126

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for vapor samples containing the chemical agent GD. No significant

method interferents have been identified. Users of this method should confirm that the test material does not offgas an interferent in the detection region of interest.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The vapor samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction of a vapor sample is performed using a MARKES Thermal Desorption System (TDS). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and MARKES Technologies. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute GD standards prepared in high purity hexane or chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for

equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

The mass of agent on tube should be estimated for vapor samples to minimize saturation of the detector.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, tube spiking, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as mass on tube (ng). Mass on tube can be calculated in the instrument control software (e.g., Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported mass is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"GDLL-Deans.M"
ECBC Decon Sciences Team
408-GCV Method Summary

INSTRUMENT CONTROL PARAMETERS: GCV (6890GC - 5975MSD)

D:\GC-MS METHODS\GDLL-DEANS.M

Control Information
------- -----------

Sample Inlet	: GC
Injection Source	: Manual
Injection Location	: Front
Mass Spectrometer	: Enabled

===

AGILENT DEANS SWITCH PARAMETERS

===

METHOD: 408-GCV_Deans.M

Comment: Deans Switch Parameters for 408-GCV w/ Markes Thermal Desorption System.

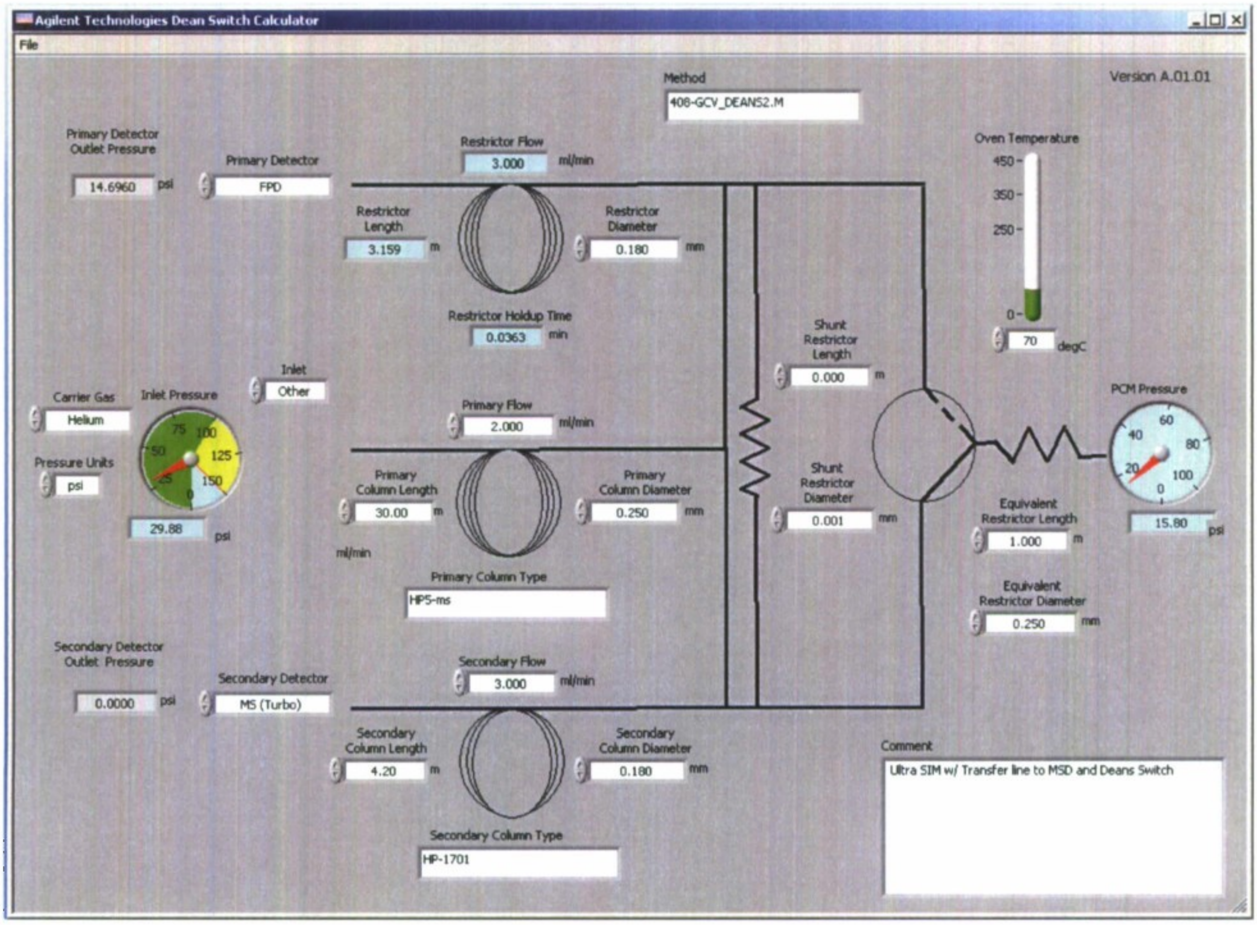
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	29.88	15.80
Avg. Linear Velocity (cm/sec):	30.58	168.85
Hold up Time (min):	1.64	0.041
Restrictor Length (m):		3.159
Restrictor Hold Up Time (min):		0.036

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	4.20
i.d. (MM):	0.25	0.25
Flow (ml/min):	2.00	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70
Restrictor Diameter:		0.18
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR

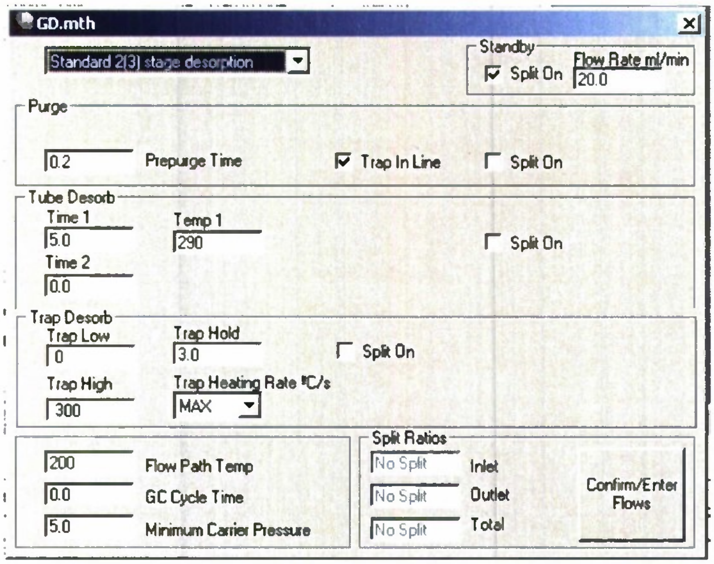


MARKES TDS UNITY METHOD

UNITY METHOD NAME = GDLL.mth

Operating Mod = Standards Two Stage
Standby Flow = 20
Purge Time = 0.2
Minimum Carrier Pressure = 5
Purge Trap in Line = TRUE
Purge Flow = 20
Oven Temperature 1 = 290
Desorb Time 1 = 5
Desorb Time 2 = 0
Desorb Tube Split = FALSE
Desorb Tube Flow = 20
Dry Purge Time = 1
Standard Injection Time = 1
Trap Low = 0

```
Trap High = 300
Trap Hold = 3
Column Flow = 0
Desorb Flow = 0
Tube Desorb Split = 0
Trap Desorb Split = 0
Inlet Split Ratio = No Split
Outlet Split Ration = No Split
Total Split Ratio = No Split
Flow Path Temperature = 200
GC Cycle Time = 0
```




```
===========================================================================
                              6890 GC METHOD
===========================================================================
OVEN
   Initial temp:  70 'C (On)                Maximum temp:  300 'C
   Initial time:  0.00 min                  Equilibration time:  0.00 min
   Ramps:
      # Rate Final temp Final time
      1 50.00      260        1.00
      2   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  4.80 min

FRONT INLET (SPLIT/SPLITLESS)            BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  250 'C (On)
   Pressure:  29.90 psi (On)
   Purge flow:  49.9 mL/min
   Purge time:  999.99 min
   Total flow:  55.5 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                 COLUMN 2
```

```
   Capillary Column                               (not installed)
   Model Number:  Agilent 19091S-433
   HP-5MS  5% Phenyl Methyl Siloxane
   Max temperature:  325 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant pressure
   Pressure:  29.90 psi
   Nominal initial flow:  3.2 mL/min
   Average velocity:  58 cm/sec
   Inlet:  Front Inlet
   Outlet:  Other
   Outlet pressure:  ambient

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
   Temperature:  250 'C (On)
   Hydrogen flow:  75.0 mL/min (On)
   Oxidizer flow:  100.0 mL/min (On)
   Oxidizer Gas Type: Air
   Mode:  Constant makeup flow
   Makeup flow:  25.0 mL/min (On)
   Makeup Gas Type: Helium
   Flame:  On
   Lit offset:  2.00
   Photo multiplier:  On

SIGNAL 1
   Data rate:  20 Hz
   Type:  back detector
   Save Data:  On
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

SIGNAL 2
   Data rate:  20 Hz
   Type:  test plot
   Save Data:  Off
   Zero:  0.0 (Off)
   Range:  0
   Fast Peaks:  Off
   Attenuation:  0

COLUMN COMP 1
   (No Detectors Installed)

COLUMN COMP 2
   (No Detectors Installed)

THERMAL AUX 1
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

THERMAL AUX 2
   Unknown Thermal Aux Type

AUX PRESSURE 3
   Description: Deans Switch
   Gas Type:  Helium
   Initial pressure:  15.80 psi (On)
   Initial time:  0.00 min
      #  Rate  Final pres  Final time
      1   0.0(Off)

AUX PRESSURE 4
   Description:
   Gas Type:  Helium
   Initial pressure:  17.60 psi (Off)

AUX PRESSURE 5
   Description:
```

```
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)

VALVES                                       POST RUN
   Valve 1  Switching Off                       Post Time: 0.00 min
      Description:

TIME TABLE
   Time        Specifier                        Parameter & Setpoint
      3.05        Valve 1:                         On
      3.35        Valve 1:                         Off
```

GC Injector

```
     Front Injector:
No parameters specified

     Back Injector:
No parameters specified

 Column 1 Inventory Number : AB002
 Column 2 Inventory Number :
```

MS ACQUISITION PARAMETERS

```
General Information
------- -----------
Tune File                 : atune.u
Acquistion Mode           : SIM


MS Information
-- -----------
Solvent Delay             : 2.50 min

EM Absolute               : False
EM Offset                 : 200
Resulting EM Voltage      : 2294.1*

[Sim Parameters]

GROUP 1
Group ID                  : GD
Resolution                : High
Plot 1 Ion                : 126.00
Ions/Dwell In Group
(Mass,  Dwell)
(69.00, 75)
(82.00, 75)
(99.00, 75)
(126.00, 75)

[MSZones]

MS Quad                   : 150 C   maximum 200 C
```

```
MS Source                : 230 C    maximum 250 C
Timed Events
----- ------

[Timed MS Detector Entries]

Time (min)          State (MS on/off)
3.00                     On
3.40                     Off

                              END OF MS ACQUISITION PARAMETERS


                                TUNE PARAMETERS*
                                -----------------
*MSD Specific Values automatically determined and set when performing an
Autotune.

END OF TUNE PARAMETERS
-----------------------
END OF INSTRUMENT CONTROL PARAMETER
```

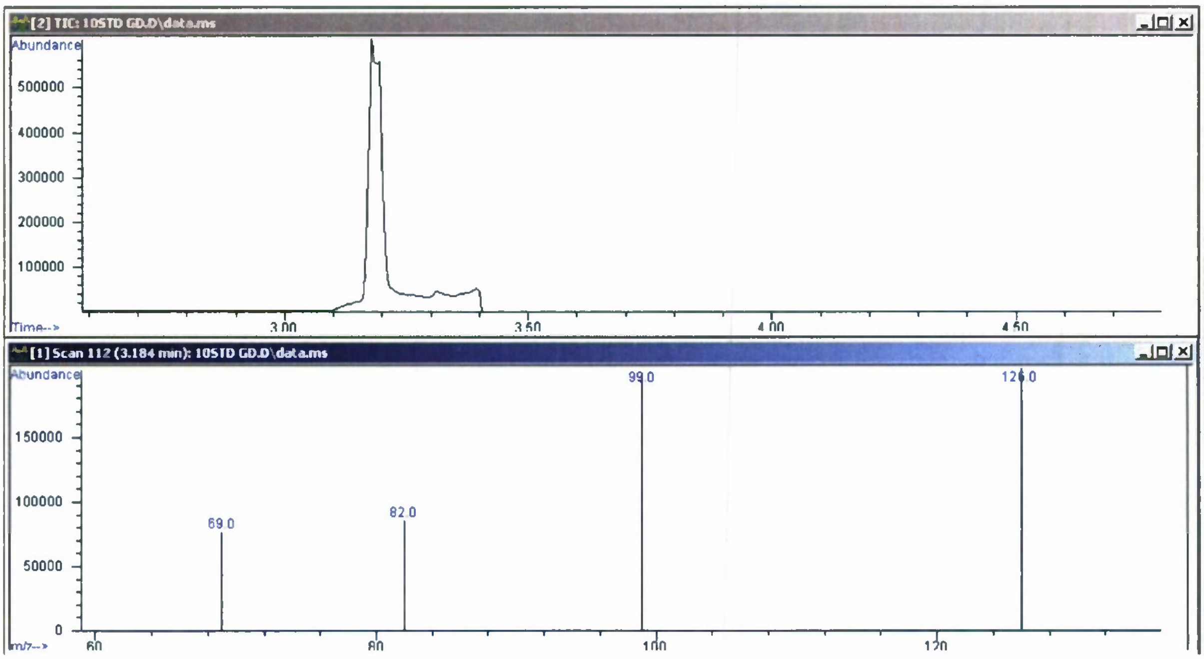
GD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Soman Formula: $C_7H_{16}FO_2P$ MW: 182
CAS#: 96-64-0 NIST#: 226124 ID#: 78999 DB: mainlib

A sample spectrum from this program is provided.

GD SPECTRUM (SIM) - 408-GCV DATA ANALYSIS



Approximate Method retention time for GD: 3.195 minutes.

METHOD I: GC-MS METHOD FOR HIGH-LEVEL GD VAPOR SAMPLE ANALYSIS (GCV GDHL-DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of GD in vapor samples for chemical agent decontamination testing using a GC/MSD with a thermal desorption unit.

AUTHORS
Morgan Hall (SAIC)
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences ECBC)

KEYWORDS
Soman, GD, O-Pinacolyl methylphosphonofluoridate; CAS 96-64-0

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent GD in vapor samples. This method is based on the collection of vapor samples on tubes containing solid sorbent material following chemical agent decontamination performance evaluation testing. The method is optimized for the detection requirements for the analysis of a 2-inch diameter test surface area. It is anticipated that this method can support larger item vapor testing. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This method is a complementary method to the low-level method for the detection of higher concentrations of GD from vapor sorbent tube samples. This GD high level method can detect GD with a mass on column range of 10.0 ng to 500 ng. Sample collection parameters are adjusted to collect vapor samples in this mass range. With this high level method a 95 mL/min split is needed with the Markes system in order to achieve these higher masses. No parameter changes are needed with the Agilent GC/MSD system.

This method utilizes five calibration standards at concentrations of 10, 25, 50, 250, and 500 ng GD. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in acetonitrile.

The method performance for GD is as follows:

- Quantitative Method
- Calibration Range: 10 to 500 ng GD on column.
- Calibration Model: linear forced zero calibration model
- Calibration Weighting: none
- Limit of Detection (LOD): 2.65 ng
- Limit of Quantitation (LOQ): 8.02 ng
- Spiking sample Solvent: acetonitrile
- Quant Ion: 126

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for vapor samples containing the chemical agent GD. No significant method interferents have been identified. Users of this method should confirm that the test material does not offgas an interferent in the detection region of interest.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The vapor samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction of a vapor sample is performed using a MARKES Thermal Desorption System (TDS). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and MARKES. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute GD standards prepared in high purity hexane or chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

The mass of agent on tube should be estimated for vapor samples to minimize saturation of the detector.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, tube spiking, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as mass on tube (ng). Mass on tube can be calculated in the instrument control software (e.g., Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported mass is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

"GDHL-Deans.M"
ECBC Decon Sciences Team
408-GCV Method Summary

INSTRUMENT CONTROL PARAMETERS: GCV (6890GC - 5975MSD)

D:\GC-MS METHODS\GDHL-DEANS.M

Control Information

Sample Inlet	GC
Injection Source	Manual
Injection Location	Front
Mass Spectrometer	Enabled

AGILENT DEANS SWITCH PARAMETERS

METHOD: 408-GCV_Deans.M

Comment: Deans Switch Parameters for 408-GCV w/ Markes Thermal Desorption System.

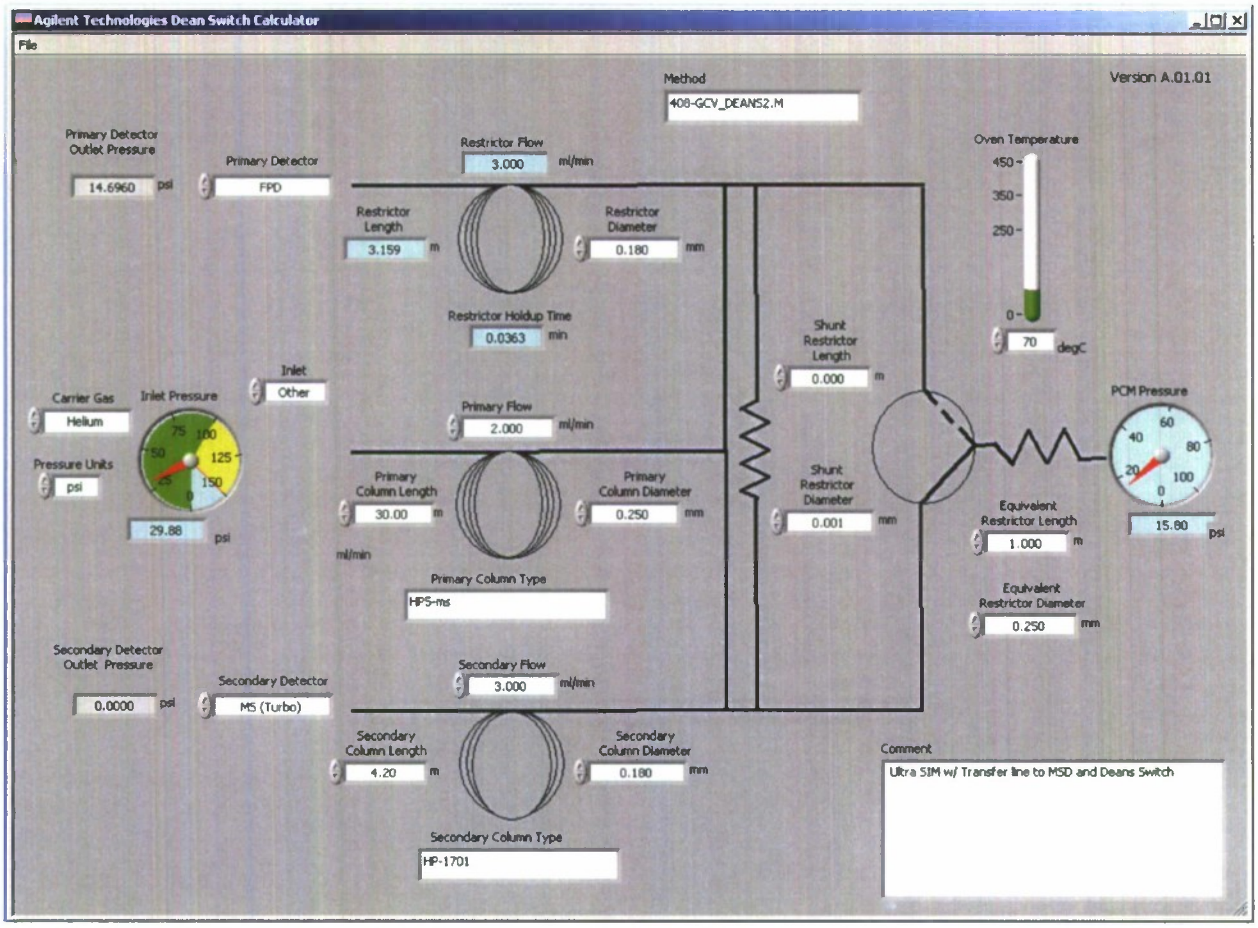
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	29.88	15.80
Avg. Linear Velocity (cm/sec):	30.58	168.85
Hold up Time (min):	1.64	0.041
Restrictor Length (m):		3.159
Restrictor Hold Up Time (min):		0.036

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	4.20
i.d. (MM):	0.25	0.25
Flow (ml/min):	2.00	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70
Restrictor Diameter:		0.18
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

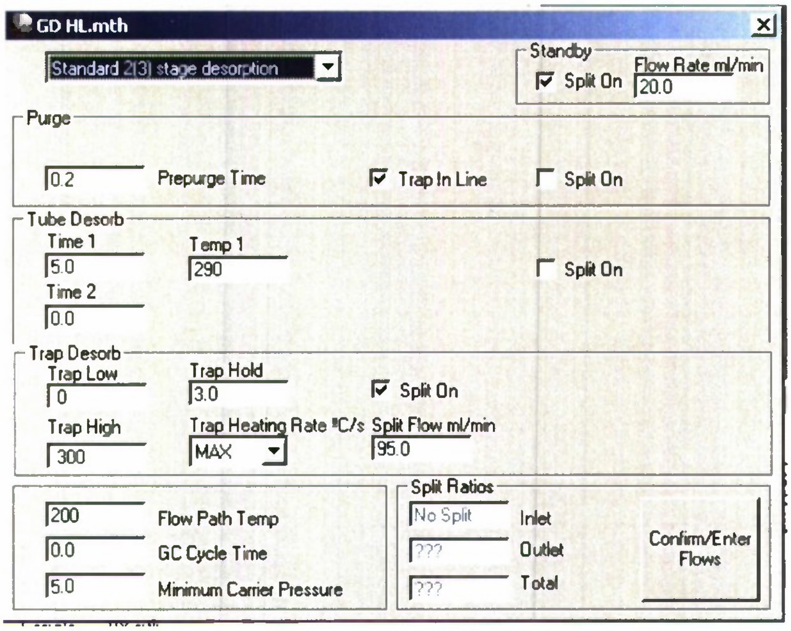
DEANS SWITCH CALCULATOR




```
===========================================================================
                         MARKES TDS UNITY METHOD
===========================================================================
UNITY METHOD NAME = GDHL.mth

Operating Mod = Standards Two Stage
Standby Flow = 20
Purge Time = 0.2
Minimum Carrier Pressure = 5
Purge Trap in Line = TRUE
Purge Flow = 20
Oven Temperature 1 = 290
Desorb Time 1 = 5
Desorb Time 2 = 0
Desorb Tube Split = FALSE
Desorb Tube Flow = 20
Dry Purge Time = 1
Standard Injection Time = 1
Trap Low = 0
Trap High = 300
Trap Hold = 3
Column Flow = 0
```

```
Desorb Flow = 0
Tube Desorb Split = 0
Trap Desorb Split = 95 ml/min
Inlet Split Ratio = No Split
Outlet Split Ration = No Split
Total Split Ratio = No Split
Flow Path Temperature = 200
GC Cycle Time = 0
```




```
======================================================================
                          6890 GC METHOD
======================================================================
OVEN
   Initial temp:  70 'C (On)                 Maximum temp:  300 'C
   Initial time:  0.00 min                   Equilibration time:  0.00 min
   Ramps:
      # Rate Final temp Final time
      1 50.00      260        1.00
      2   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  4.80 min

FRONT INLET (SPLIT/SPLITLESS)              BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  250 'C (On)
   Pressure:  29.90 psi (On)
   Purge flow:  49.9 mL/min
   Purge time:  999.99 min
   Total flow:  55.5 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                   COLUMN 2
```

Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 29.90 psi
Nominal initial flow: 3.2 mL/min
Average velocity: 58 cm/sec
Inlet: Front Inlet
Outlet: Other
Outlet pressure: ambient

(not installed)

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description:
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: Deans Switch
Gas Type: Helium
Initial pressure: 15.80 psi (On)
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

AUX PRESSURE 4
Description:
Gas Type: Helium
Initial pressure: 17.60 psi (Off)

AUX PRESSURE 5
Description:

```
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)

VALVES                                    POST RUN
   Valve 1  Switching Off                    Post Time: 0.00 min
      Description:

TIME TABLE
   Time       Specifier                     Parameter & Setpoint
      3.05       Valve 1:                      On
      3.35       Valve 1:                      Off
                                    GC Injector


     Front Injector:
No parameters specified

     Back Injector:
No parameters specified

 Column 1 Inventory Number : AB002
 Column 2 Inventory Number :


                               MS ACQUISITION PARAMETERS

General Information
------- -----------
Tune File                 : atune.u
Acquistion Mode           : SIM


MS Information
-- -----------
Solvent Delay             : 2.50 min

EM Absolute               : False
EM Offset                 : 200
Resulting EM Voltage      : 2294.1*

[Sim Parameters]

GROUP 1
Group ID                  : GD
Resolution                : High
Plot 1 Ion                : 99.00
Ions/Dwell In Group
(Mass,  Dwell)
(69.00, 75)
(82.00, 75)
(99.00, 75)
(126.00, 75)

[MSZones]

MS Quad                   : 150 C   maximum 200 C
MS Source                 : 230 C   maximum 250 C
```

```
Timed Events
----- ------

[Timed MS Detector Entries]

Time (min)          State (MS on/off)
3.00                     On
3.40                     Off
```

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS*

*MSD Specific Values automatically determined and set when performing an Autotune.

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETER

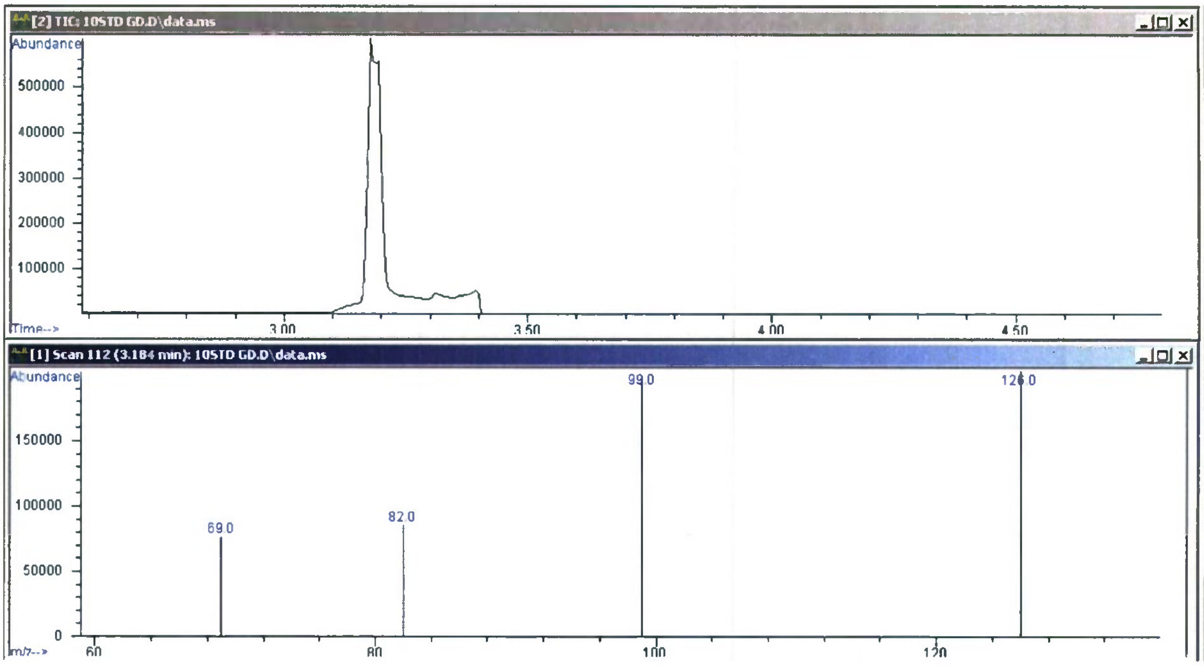
GD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Soman Formula: $C_7H_{16}FO_2P$ MW: 182
CAS#: 96-64-0 NIST#: 226124 ID#: 78999 DB: mainlib

A sample spectrum from this program is provided.

GD SPECTRUM (SIM) - 408-GCV DATA ANALYSIS



Approximate Method retention time for GD: 3.195 minutes.

METHOD J: GC/MS METHOD FOR LOW-LEVEL HD (GCE HD_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of HD in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with Autosampler.

AUTHORS
Matt Shue (SAIC)
Zach Zander (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Mustard, HD, Bis(2-chloroethyl)sulfide CAS 505-60-2

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent HD in liquid extraction samples. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This method can detect HD solution concentrations from 2.0 to 2000 ng/mL. This method has two intended uses based upon the method capabilities. For confidence across the entire concentration range, the method will be used as an ultra-low level method with a concentration range spanning 2.5 – 25 ng/mL and as a low level method with a concentration range spanning 25 – 2000 ng/mL.

This method utilizes thirteen calibration standards at concentrations of 2, 5, 10, 25, 50, 100, 150, 200, 250, 500, 750, 1000, and 2000 ng/ml HD. The method use, detection limit and quantitation limit are based on using the full standard set. The standards are prepared in chloroform.

The method performance for HD-LL is as follows:

- Quantitative Method
- Calibration range: 2.5 to 50 ng/mL HD
- Calibration model: quadratic calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 1.50 ng
- Limit of Quantitation (LOQ): 4.56 ng
- Sample Solvent: chloroform
- Quant Ion: 111

The method performance for HD-HL is as follows:

- Quantitative Method
- Calibration range: 25 to 2000 ng/mL HD
- Calibration model: quadratic calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 4.62 ng
- Limit of Quantitation (LOQ): 14.00 ng
- Sample Solvent: chloroform
- Quant Ion: 111

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for liquid samples extracted with the solvent chloroform ($CHCl_3$; CAS #67-66-3) and containing the chemical agent HD. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4).

The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane. column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute HD standards prepared in high purity chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the

specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

408-GCE Method Summary

INSTRUMENT CONTROL PARAMETERS: GCE (6890GC - 5975MSD)

D:\GC-MS METHODS\HD_Deans.M

Control Information

Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes

AGILENT DEANS SWITCH PARAMETERS

METHOD: 408-GCE_Deans.M

Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.

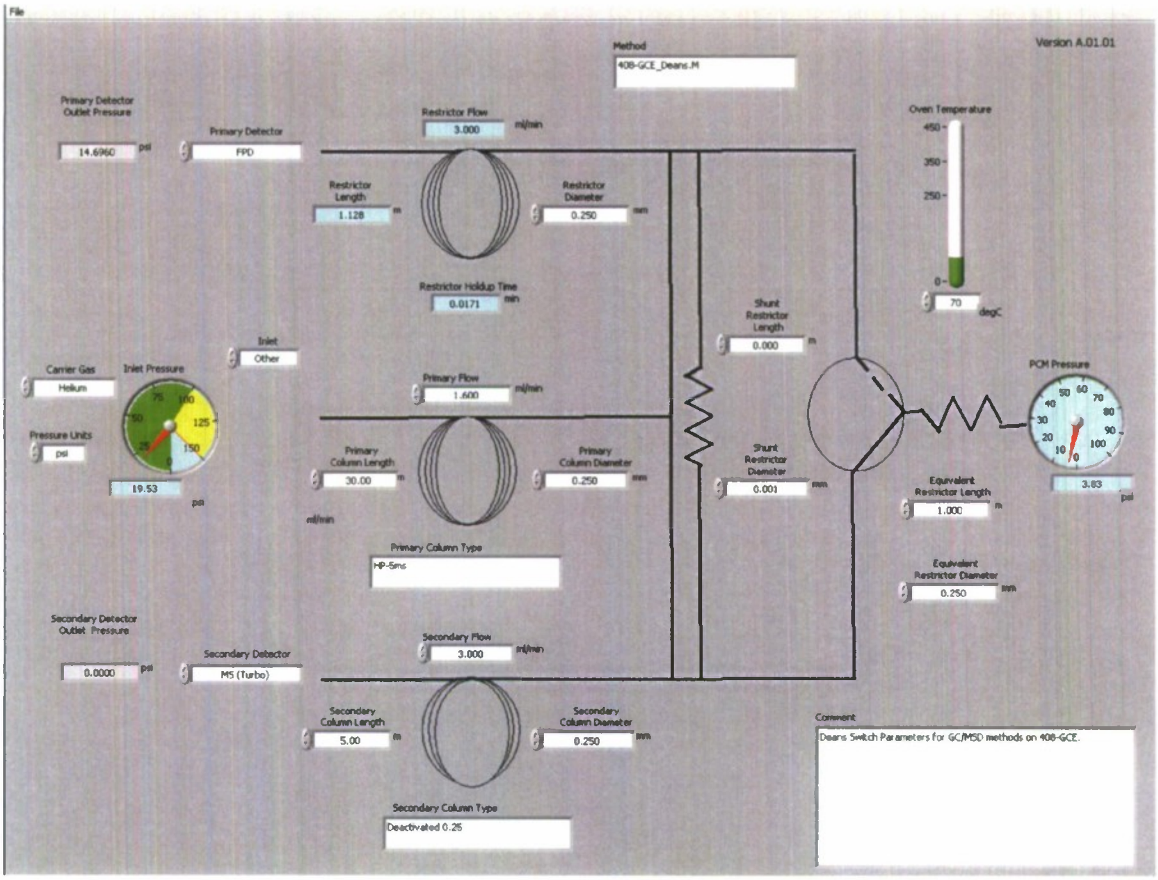
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	19.53	3.83
Avg. Linear Velocity (cm/sec):	34.72	154.76
Hold up Time (min):	1.44	0.054
Restrictor Length (m):		1.128
Restrictor Hold Up Time (min):		0.017

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	5.00
i.d. (MM):	0.25	0.25
Flow (ml/min):	1.60	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70.00
Restrictor Diameter:		0.25
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR



==

GERSTEL CIS

==

```
TEMPERATURE PROGRAM
Initial Temperature        : 10 'C
Equilibration Time         : 0.05 min
Initial Time               : 0.20 min
Ramp 1
Rate 1                : 10.0 'C/s
End Temp 1            : 280 'C
Hold Time 1           : 3.00 min
Ramp 2
Rate 2                : 0.0 'C/s

CRYO COOLING
Cryo Cooling               : used

GERSTEL MPS Liquid Injection

Syringe                    : 10ul
```

```
SAMPLE PARAMETERS
Inj. Volume              : 2.0 uL
Inj. Speed               : 25.00 uL/s
Fill Volume              : 10.0 uL
Fill Strokes             : 3

Fill Speed               : 5.00 uL/s
Eject Speed              : 100.00 uL/s
Viscositiy Delay         : 1.0 s

Air Volume               : 0.0 uL
Pre Inj. Delay           : 0.00 s
Post Inj. Delay          : 0.00 s
Inj. Penetration         : 40.00 mm
Vial Penetration         : 31.00 mm

CLEANING PARAMETERS
Preclean Sample          : 0

Preclean Solv.1          : 1
Postclean Solv.1         : 3
Fill Speed Solv.1        : 5.00 uL/s
Viscosity Delay Solv.1   : 1.0 s
Eject Speed Solv.1       : 100.00 uL/s

Preclean Solv.2          : 1
Postclean Solv.2         : 3
Fill Speed Solv.2        : 5.00 uL/s
Viscosity Delay Solv.2   : 1.0 s
Eject Speed Solv.2       : 100.00 uL/s

===========================================================================
                              6890 GC METHOD
===========================================================================
OVEN
Initial temp:  70 'C (On)                Maximum temp:  325 'C
Initial time:  0.75 min                  Equilibration time:  0.25 min
Ramps:
#  Rate  Final temp  Final time
1 35.00     120        0.00
2 10.00     150        0.00
3 40.00     300        1.07
4   0.0(Off)
Post temp:  70 'C
Post time:  0.00 min
Run time:  10.00 min

FRONT INLET (SPLIT/SPLITLESS)            BACK INLET (CIS3)
Mode:  Split                             Mode:  Solvent Vent
Initial temp:  200 'C (Off)              Initial temp:  250 'C (Off)
Pressure:  0.00 psi (Off)                Pressure:  19.53 psi (On)
Total flow:  3.7 mL/min                  Vent time:  0.20 min
Gas saver:  Off                          Vent flow:  20.0 mL/min
Gas type:  Helium                        Vent Pressure:  19.5 psi
                                          Purge flow:  50.0 mL/min
```

Purge time: 3.00 min
Total flow: 54.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium
Initial pressure: 3.80 psi (On)

```
                                         Initial time:  0.00 min
                                          #  Rate  Final pres  Final time
                                          1   0.0(Off)

AUX PRESSURE 5
Description:
Gas Type:  Helium
Initial pressure:  0.00 psi (Off)

VALVES                                   POST RUN
Valve 1  Switching Off                   Post Time: 0.00 min
Description:

TIME TABLE
Time       Specifier                      Parameter & Setpoint
5.10       Valve 1:                       On
6.10       Valve 1:                       Off


GC Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number : AB001
Column 2 Inventory Number : AB002


=============================================================================
                       5975 MS ACQUISITION PARAMETERS
=============================================================================
General Information
------- -----------
Tune File                  : atune.u
Acquistion Mode            : SIM

MS Information
-- -----------
Solvent Delay              : 5.00 min

EM Absolute                : False
EM Offset                  : 400
Resulting EM Voltage       : 2400.0*

[Sim Parameters]

GROUP 1
Group ID                   : HD
Resolution                 : High
Plot 1 Ion                 : 109.00
Ions/Dwell In Group:
```

```
(Mass, Dwell)
(109.00, 50)
(111.00, 50)
(158.00, 50)
(160.00, 50)

[MSZones]

MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C
Timed Events
----- ------

[Timed MS Detector Entries]

END OF MS ACQUISITION PARAMETERS

                               TUNE PARAMETERS*
                               ---------------
```

MSD Specific Values automatically determined and set when performing an Autotune.

```
END OF TUNE PARAMETERS
------------------------------------

END OF INSTRUMENT CONTROL PARAMETERS
---------------------------------
```

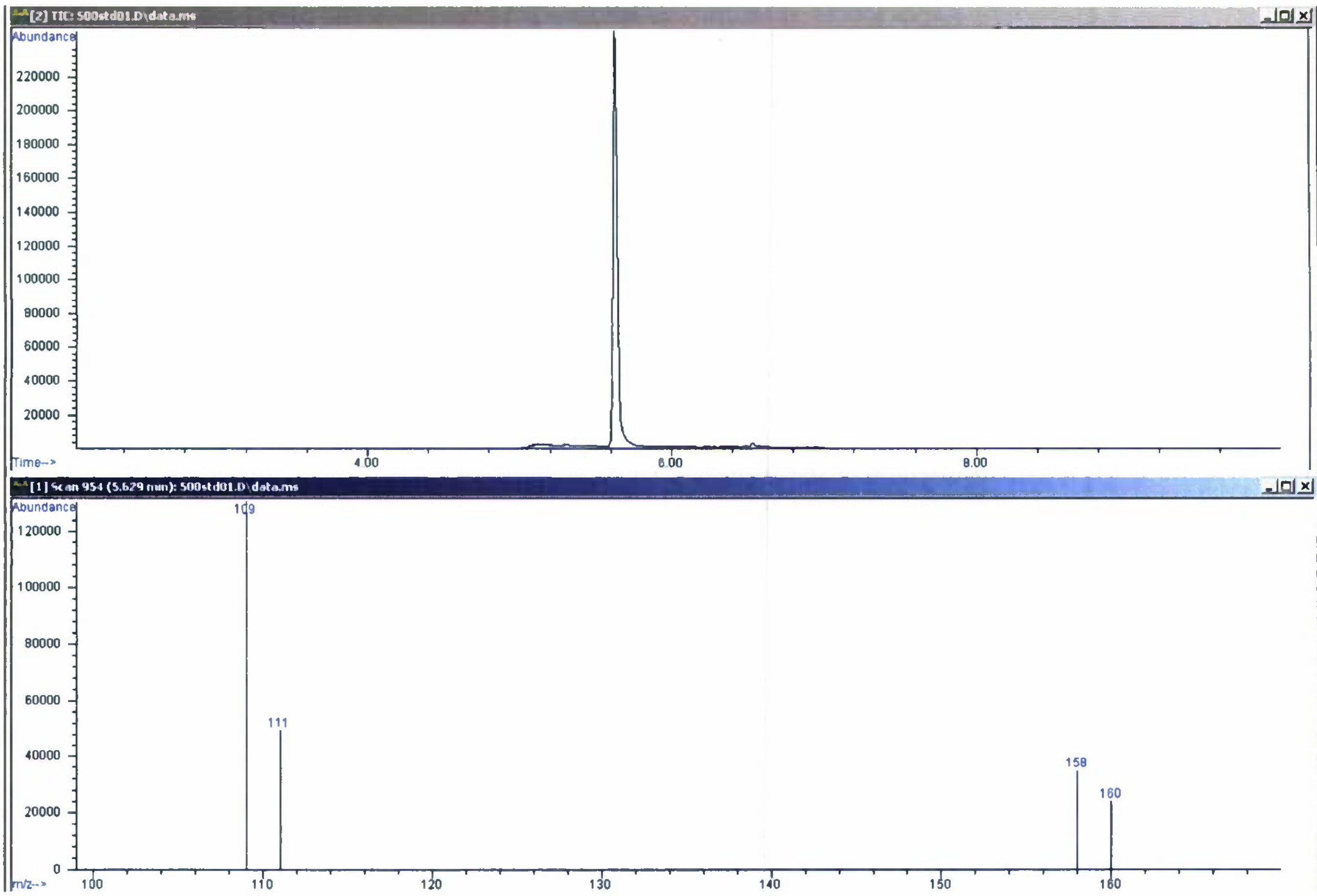
HD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

> Name: Mustard Gas Formula: $C_4H_8Cl_2S$ MW: 158
> CAS#: 505-60-2 NIST#: 289463 ID#: 65664 DB: mainlib

A sample spectrum from this program is provided.

HD TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



Approximate Method retention time for HD: 5.63 minutes.

METHOD K: GC/MS METHOD FOR LOW-LEVEL GD (GCE GD_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of GD in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with Autosampler.

AUTHORS
Matt Shue (SAIC)
Michelle Sheahy (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Soman, GD, O-Pinacolyl methylphosphonofluoridate CAS 69-64-0

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and quantify the chemical agent GD in liquid extraction samples. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately eight (8) samples per hour.

ANALYTE CONCENTRATION RANGE
This method can detect GD solution concentrations from 2.5 to 2000 ng/mL. This method has two intended uses based upon the method capabilities. For confidence across the entire concentration range, the method will be used as an ultra-low level method with a concentration range spanning 2.5 – 50 ng/mL and as a low level method with a concentration range spanning 50 – 2000 ng/mL.

This method utilizes eleven calibration standards at concentrations of 2.5, 5, 10, 25, 50, 100, 250, 500, 750, 1000, and 2000 ng/mL GD. The method use, detection limit and quantitation limit are based on using the full standard set. The solvents are prepared in acetonitrile.

The method performance for GD is as follows:

- Quantitative Method
- Calibration range: 2.5 to 50 ng/mL GD.
- Calibration model: linear (with intercept) regression calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 1.52 ng/mL
- Limit of Quantitation (LOQ): 4.61 ng/mL
- Sample Solvent: acetonitrile
- Quant Ion: 126

The method performance for GD is as follows:

- Quantitative Method

- Calibration range: 50 to 2000 ng/mL GD.
- Calibration model: quadratic calibration model
- Calibration weighting: none
- Limit of Detection (LOD): 27.13 ng/mL
- Limit of Quantitation (LOQ): 82.22 ng/mL
- Sample Solvent: acetonitrile
- Quant Ion: 126

SAMPLE MATRICES AND INTERFERENCES

This method is appropriate for liquid samples extracted with the solvent Acetonitrile (CH_3CN; CAS #75-05-8) and containing the chemical agent GD. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT

This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Applied Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute GD standards prepared in high purity acetonitrile solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in

the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
INSTRUMENT CONTROL PARAMETERS:    GCE (6890GC - 5975MSD)
--------------------------------------------------------
D:\GC-MS METHODS\GD_Deans.M

Control Information
------- -----------
Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes


=========================================================================
                    AGILENT DEANS SWITCH PARAMETERS
=========================================================================
METHOD: 408-GCE_Deans.M

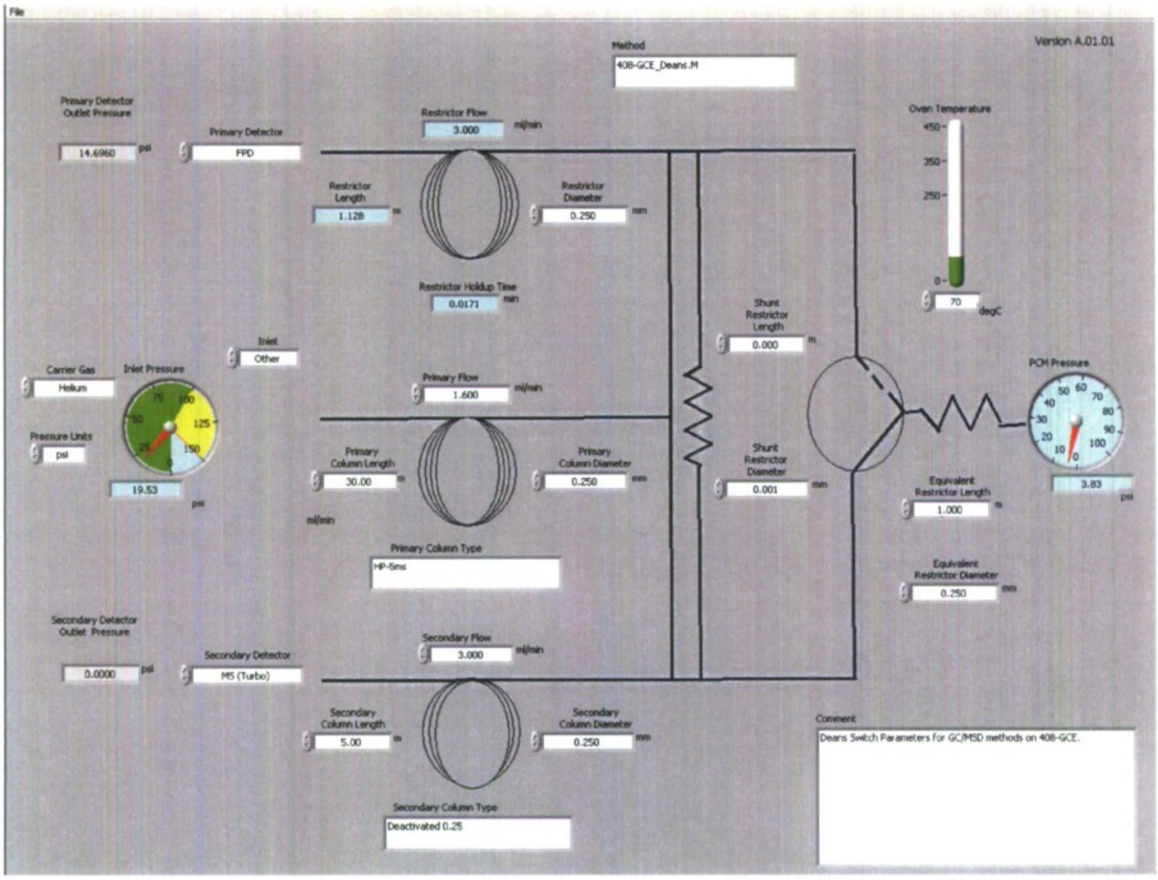
     Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.

CALCULATION RESULTS:
                                  Primary Column   Secondary Column
Inlet Pressure:                        19.53            3.83
   Avg. Linear Velocity (cm/sec):      34.72            154.76
   Hold up Time (min):                 1.44             0.054

Restrictor Length (m):                                  1.128
   Restrictor Hold Up Time (min):                       0.017

CALCULATION INPUTS
                                  Primary Column   Secondary Column
Length (m):                            30.00            5.00
i.d. (MM):                              0.25            0.25
Flow (ml/min):                          1.60            3.00
Detector:                              FPD              MS (Turbo)
Detector Pressure (abs):               14.70            0.00
Carrier Gas:                                            Helium
Pressure Units:                                         psi
Oven Temperature:                                       70.00
Restrictor Diameter:                                    0.25
Equivalent Restrictor Diameter (mm):                    0.25
Equivalent Restrictor Length (m):                       1.000


                         DEANS SWITCH CALCULATOR
                        ------------------------
```




```
================================================================================
                                   GERSTEL CIS
================================================================================
TEMPERATURE PROGRAM
Initial Temperature        : 50 'C
Equilibration Time         : 0.05 min
Initial Time               : 0.20 min
Ramp 1
Rate 1                 : 12.0 'C/s
End Temp 1             : 280 'C
Hold Time 1            : 3.00 min
Ramp 2
Rate 2                 : 0.0 'C/s

CRYO COOLING
Cryo Cooling               : used


GERSTEL MPS Liquid Injection

Syringe                    : 10ul

SAMPLE PARAMETERS
Inj. Volume                : 1.0 uL
Inj. Speed                 : 25.00 uL/s
Fill Volume                : 10.0 uL
```

```
Fill Strokes            : 3

Fill Speed              : 5.00 uL/s
Eject Speed             : 100.00 uL/s
Viscositiy Delay        : 1.0 s

Air Volume              : 0.0 uL
Pre Inj. Delay          : 0.00 s
Post Inj. Delay         : 0.00 s
Inj. Penetration        : 40.00 mm
Vial Penetration        : 31.00 mm

CLEANING PARAMETERS
Preclean Sample         : 0

Preclean Solv.1         : 1
Postclean Solv.1        : 2
Fill Speed Solv.1       : 5.00 uL/s
Viscosity Delay Solv.1  : 1.0 s
Eject Speed Solv.1      : 100.00 uL/s

Preclean Solv.2         : 1
Postclean Solv.2        : 2
Fill Speed Solv.2       : 5.00 uL/s
Viscosity Delay Solv.2  : 1.0 s
Eject Speed Solv.2      : 100.00 uL/s

===========================================================================
                               6890 GC METHOD
===========================================================================

OVEN
   Initial temp:  70 'C (On)               Maximum temp:  325 'C
   Initial time:  0.75 min                 Equilibration time:  0.25 min
   Ramps:
      #  Rate  Final temp  Final time
      1 45.00     260        1.00
      2   0.0(Off)
   Post temp:  50 'C
   Post time:  0.00 min
   Run time:  5.97 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (CIS3)
   Mode:  Split                            Mode:  Solvent Vent
   Initial temp:  200 'C (Off)             Initial temp:  250 'C (Off)
   Pressure:  0.00 psi (Off)               Pressure:  19.53 psi (On)
   Total flow:  3.7 mL/min                 Vent time:  0.20 min
   Gas saver:  Off                         Vent flow:  20.0 mL/min
   Gas type:  Helium                       Vent Pressure:  19.5 psi
                                           Purge flow:  50.0 mL/min
                                           Purge time:  3.00 min
                                           Total flow:  54.4 mL/min
                                           Gas saver:  Off
                                           Gas type:  Helium
```

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium
Initial pressure: 3.80 psi (On)
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

AUX PRESSURE 5

```
   Description:
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)

VALVES                                     POST RUN
   Valve 1  Switching On                      Post Time: 0.00 min
      Description:

TIME TABLE
   Time       Specifier                     Parameter & Setpoint
      3.30       Valve 1:                        On
      4.30       Valve 1:                        Off


=============================================================================
                       5975 MS ACQUISITION PARAMETERS
=============================================================================
General Information
------- -----------

Tune File                  : atune.u
Acquistion Mode            : SIM

MS Information
-- -----------

Solvent Delay              : 3.00 min
EM Absolute                : False
EM Offset                  : 400
Resulting EM Voltage       : 2400.0*

[Sim Parameters]

GROUP 1
Group ID                   : GD
Resolution                 : High
Plot 1 Ion                 : 126.00

Ions/Dwell In Group

(Mass, Dwell)

(69.00, 75)**
(82.00, 75)
(99.00, 75)
(126.00, 75)

**Ion 69.00 is collected in the method but not used for quantification.

[MSZones]
MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C

END OF MS ACQUISITION PARAMETERS
```

TUNE PARAMETERS*
----

*MSD Specific Values automatically determined and set when performing an Autotune.

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

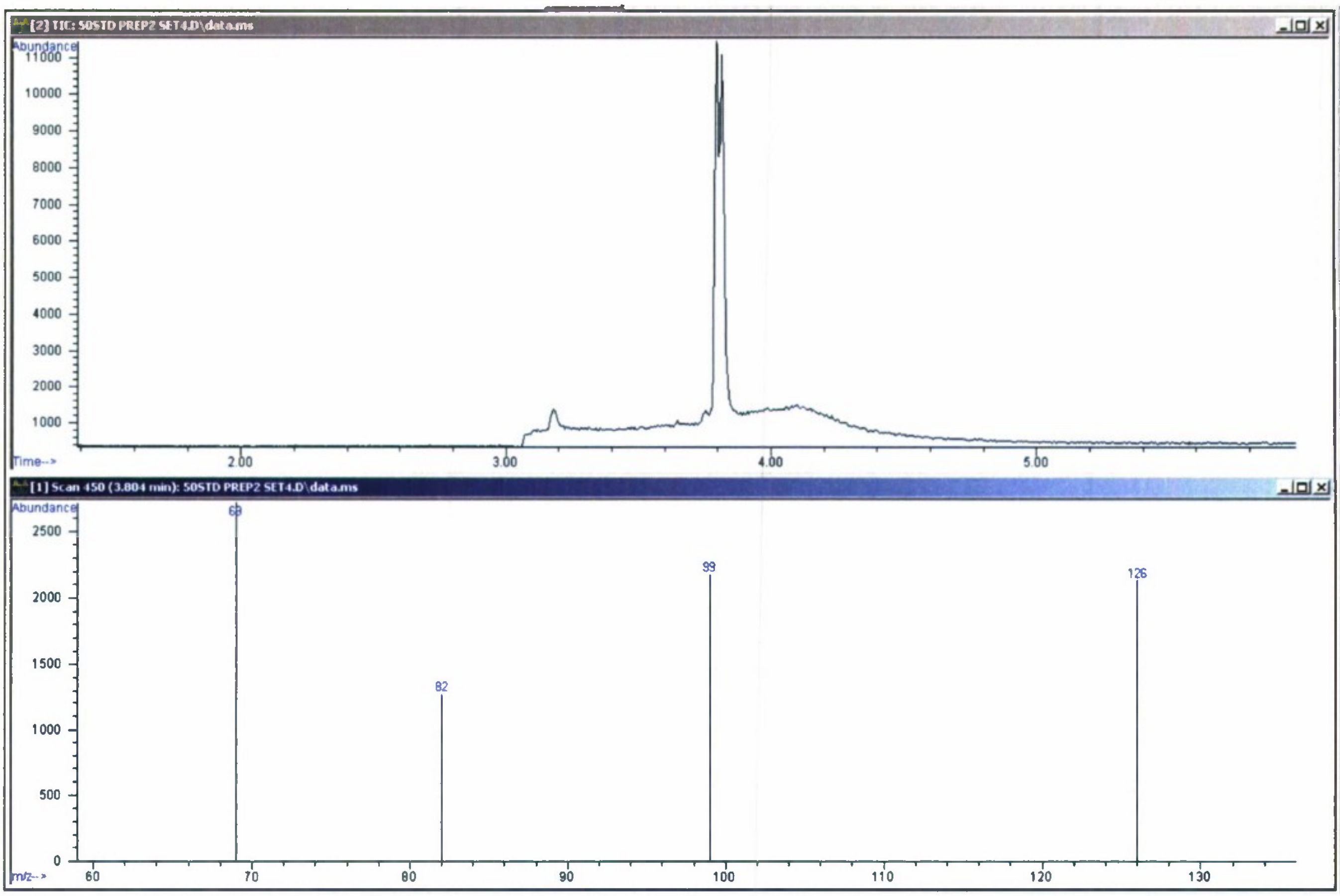
GD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Soman Formula: $C_7H_{16}FO_2P$ MW: 182
CAS#: 96-64-0 NIST#: 226124 ID#: 78999 DB: mainlib

A sample spectrum from this program is provided.

GD TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



Approximate Method retention time for GD: 3.80 minutes.

METHOD L: GC-MS METHOD FOR TDG IDENTIFICATION(GCE TDG_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of the hydrolysis by-product of HD, Thiodiglycol (TDG) in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with Autosampler.

AUTHORS
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Thiodiglycol, 2,2'-Thiodiethanol CAS 111-48-8

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and identify the hydrolysis by-product of HD, Thiodiglycol (TDG), in liquid extraction samples. This method is to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately five (5) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to identify the HD by-product TDG. This method can detect and identify TDG solution concentrations from approximately 25,000 to 100,000 ng/mL. NOTE: Due to the large concentrations required, this method is not appropriate for analyzing HD and TDG simultaneously.

The method performance for TDG is as follows:
- Qualitative Method
- Sample Solvent: chloroform.
- Quant Ion: 61.

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent chloroform ($CHCl_3$; CAS #67-66-3) and containing the HD by-product Thiodiglycol. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT
This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of

generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte(s) of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute Thiodiglycol standards prepared in high purity chloroform solvent.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                           "TDG_Deans.M"
                      ECBC Decon Sciences Team
                       408-GCE Method Summary

       INSTRUMENT CONTROL PARAMETERS:    GCE (6890GC - 5975MSD)
       --------------------------------------------------------

D:\GC-MS METHODS\TDG_Deans.M

Control Information
------- -----------
Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes


=========================================================================
                     AGILENT DEANS SWITCH PARAMETERS
=========================================================================
METHOD: 408-GCE_Deans.M

     Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.

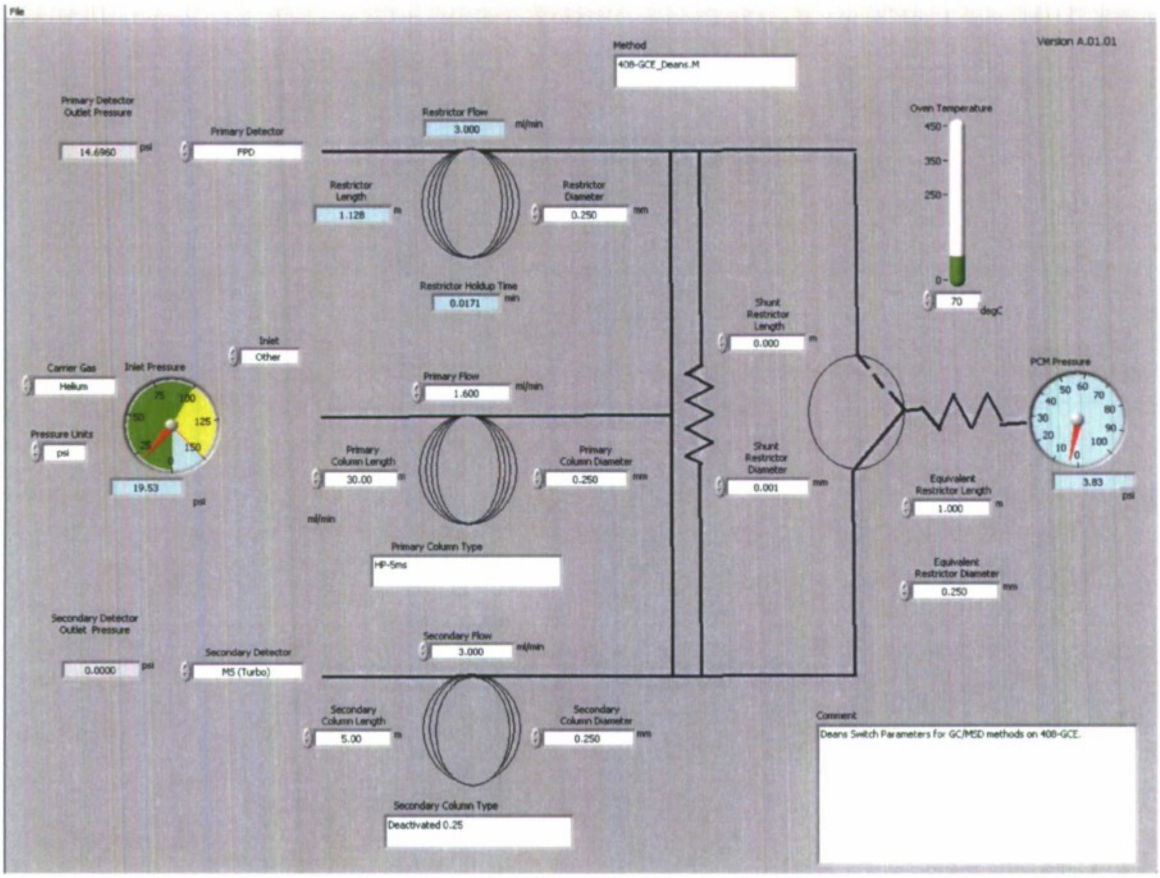
CALCULATION RESULTS:
```

	Primary Column	Secondary Column
Inlet Pressure:	19.53	3.83
Avg. Linear Velocity (cm/sec):	34.72	154.76
Hold up Time (min):	1.44	0.054
Restrictor Length (m):		1.128
Restrictor Hold Up Time (min):		0.017

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	5.00
i.d. (MM):	0.25	0.25
Flow (ml/min):	1.60	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70.00
Restrictor Diameter:		0.25
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR



==

GERSTEL CIS

==

TEMPERATURE PROGRAM
Initial Temperature : 10 'C
Equilibration Time : 0.05 min
Initial Time : 0.20 min
Ramp 1
Rate 1 : 10.0 'C/s
End Temp 1 : 280 'C
Hold Time 1 : 3.00 min
Ramp 2
Rate 2 : 0.0 'C/s

CRYO COOLING
Cryo Cooling : used

GERSTEL MPS Liquid Injection

Syringe : 10ul

```
SAMPLE PARAMETERS
Inj. Volume              : 2.0 uL
Inj. Speed               : 25.00 uL/s
Fill Volume              : 10.0 uL
Fill Strokes             : 3

Fill Speed               : 5.00 uL/s
Eject Speed              : 100.00 uL/s
Viscositiy Delay         : 1.0 s

Air Volume               : 0.0 uL
Pre Inj. Delay           : 0.00 s
Post Inj. Delay          : 0.00 s
Inj. Penetration         : 40.00 mm
Vial Penetration         : 31.00 mm

CLEANING PARAMETERS
Preclean Sample          : 0

Preclean Solv.1          : 1
Postclean Solv.1         : 3
Fill Speed Solv.1        : 5.00 uL/s
Viscosity Delay Solv.1   : 1.0 s
Eject Speed Solv.1       : 100.00 uL/s

Preclean Solv.2          : 1
Postclean Solv.2         : 3
Fill Speed Solv.2        : 5.00 uL/s
Viscosity Delay Solv.2   : 1.0 s
Eject Speed Solv.2       : 100.00 uL/s

===========================================================================
                              6890 GC METHOD
===========================================================================
OVEN
Initial temp:  70 'C (On)              Maximum temp:  325 'C
Initial time:  0.00 min                Equilibration time:  0.25 min
Ramps:
#  Rate  Final temp  Final time
1 35.00      280        1.00
2 0.00       000        0.00
3 0.00       000        0.00
4   0.0(Off)
Post temp:  70 'C
Post time:  0.00 min
Run time:   7.00 min

FRONT INLET (SPLIT/SPLITLESS)          BACK INLET (CIS3)
Mode:  Split                           Mode:  Solvent Vent
Initial temp:  200 'C (Off)            Initial temp:  250 'C (Off)
Pressure:  0.00 psi (Off)              Pressure:  19.53 psi (On)
Total flow:  3.7 mL/min                Vent time:  0.20 min
Gas saver:  Off                        Vent flow:  20.0 mL/min
Gas type:  Helium                      Vent Pressure:  19.5 psi
```

Purge flow: 50.0 mL/min
Purge time: 3.00 min
Total flow: 54.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
  Temperature: 250 'C (On)
  Hydrogen flow: 75.0 mL/min (On)
  Oxidizer flow: 100.0 mL/min (On)
  Oxidizer Gas Type: Air
  Mode: Constant makeup flow
  Makeup flow: 25.0 mL/min (On)
  Makeup Gas Type: Helium
  Flame: On
  Lit offset: 2.00
  Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium

Initial pressure: 0.00 psi (Off)

Initial pressure: 3.80 psi (On)
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

AUX PRESSURE 5
Description:
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

VALVES
Valve 1 Switching Off
Description:

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
3.90	Valve 1:	On
4.90	Valve 1:	Off

GC Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number : AB001
Column 2 Inventory Number : AB002

===

5975 MS ACQUISITION PARAMETERS

===

General Information
------- -----------

Tune File : atune.u
Acquistion Mode : SIM

MS Information
-- -----------

Solvent Delay : 3.50 min

EM Absolute : False
EM Offset : 400
Resulting EM Voltage : 2400.0*

[Sim Parameters]

GROUP 1
Group ID : TDG
Resolution : High
Plot 1 Ion : 61.00
Ions/Dwell In Group:

(Mass, Dwell)

```
(45.00, 50)
(61.00, 50)
(91.00, 50)
(104.00, 50)
(122.00, 50)

[MSZones]
MS Quad                   : 150 C   maximum 200 C
MS Source                 : 230 C   maximum 250 C
Timed Events
----- ------
[Timed MS Detector Entries]

END OF MS ACQUISITION PARAMETERS

                              TUNE PARAMETERS*
                              ---------------
```

*MSD Specific Values automatically determined and set when performing an Autotune.

```
END OF TUNE PARAMETERS
------------------------------------
END OF INSTRUMENT CONTROL PARAMETERS
---------------------------------
```

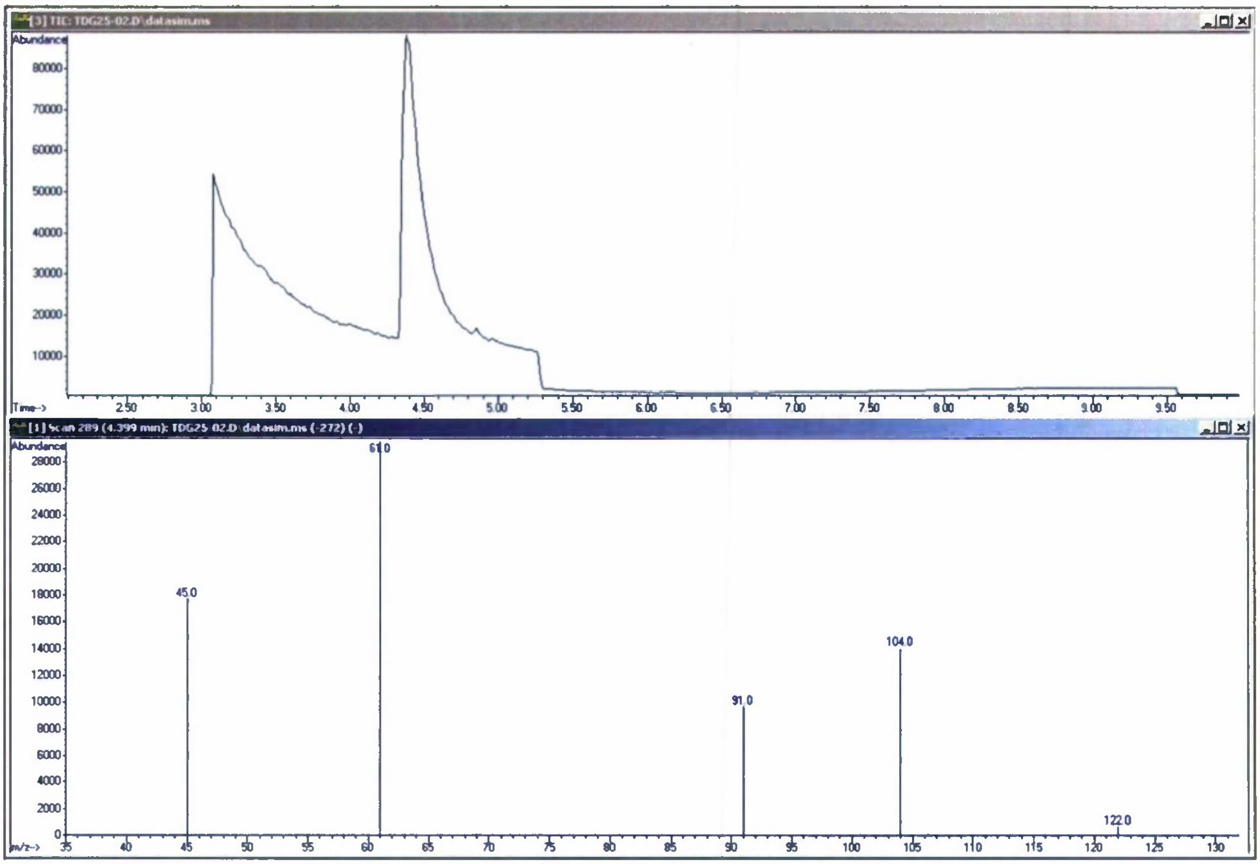
Thiodiglycol (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Thiodiglycol Formula: $C_4H_{10}O_2S$ MW: 122
CAS#: 111-48-8 NIST#: 229583 ID#: 25714 DB: mainlib

A sample spectrum from this program is provided.

TDG TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



Approximate Method retention time for TDG: 4.39 minutes.

METHOD M: LC-MS METHOD FOR HD SULFOXIDE IDENTIFICATION (LCE H-SULFIXOIDE.DAM)

ANALYTICAL METHOD

TITLE
Detection of Mustard Sulfoxide (H-Sulfoxide), an oxidation product of HD, in liquid extraction samples from chemical agent decontamination testing using an LC-MS/MS system.

AUTHORS
Matt Shue (SAIC)
Phil Smith, Ph.D. (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Mustard Sulfoxide, H-Sulfoxide, Bis(2-chloroethyl) sulfoxide, CAS 5819-08-9

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect Mustard sulfoxide (H-Sulfoxide). H-Sulfoxide is an oxidation by-product of the chemical agent HD. This method is to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately seven (7) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to screen for a HD byproduct, H-Sulfoxide. The approximate concentration range for this method is from 10.0 to 500 ng/mL.

The method performance for H-Sulfoxide is as follows:

- Qualitative Method
- Sample Solvent: chloroform.
- Quant Ion: 175 / 63.

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent chloroform ($CHCl_3$; CAS #67-66-3) and suspected to contain the HD byproduct H-Sulfoxide. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT
This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other

regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on liquid chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Applied Biosystems API5000 Triple-quadrupole Mass Spectrometer equipped with the TurboV Ion Source. Sample introduction and chromatography are performed with an Agilent 1200 series liquid chromatograph (LC). Sample effluent is directed from the LC directly to the TurboV ion source of the API5000 MS. The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Applied Biosystems and Agilent Technologies. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute standard of H-Sulfoxide prepared in high purity chloroform solvent within the working concentration range of this method.

Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                     "LCE H-Sulfoxide"
                  ECBC Decon Sciences Team
                  408-LCE Method Summary


   INSTRUMENT CONTROL PARAMETERS:    LCE (1200 Series LC / API5000 MS)
   -------------------------------------------------------------

D:\Analyst Data\Projects\HD Analysis\HD Method Development\Acquisition
Methods

Acquisition Method Properties
------- --------------------
Comment:    LC/MS/MS Method (MRM)for H-Sulfoxide.

Synchronization Mode:          LC Sync
Auto-Equilibration:            Off
Acquisition Duration:          7min0sec
Number Of Scans:               683
Periods In File:               1
Acquisition Module:            Acquisition Method
Software version:              Analyst 1.4.2

===================================================================
```

API5000 Mass Spec

==

MS Method Properties:
Period 1:

Scans in Period: 683
Relative Start Time: 0.00 msec
Experiments in Period: 1

Period 1 Experiment 1:

Scan Type: MRM (MRM)
Polarity: Positive
Scan Mode: N/A
Ion Source: Turbo Spray
Resolution Q1: Unit
Resolution Q3: High
Intensity Thres.: 0.00 cps
Settling Time: 0.0000 msec
MR Pause: 5.0070 msec
MCA: No
Step Size: 0.00 amu

@Q1 Mass (amu)	Q3 Mass (amu)	Dwell(msec)	Param	Start	Stop
175.00	63.00	200.00			

@Q1 Mass (amu)	Q3 Mass (amu)	Dwell(msec)	Param	Start	Stop
175.00	95.00	200.00			

@Q1 Mass (amu)	Q3 Mass (amu)	Dwell(msec)	Param	Start	Stop
177.00	63.00	200.00			

Parameter Table(Period 1 Experiment 1):
CUR: 15.00
GS1: 50.00
GS2: 55.00
TEM: 500.00
ihe: ON
CAD: 3.00
IS: 5500.00
DP 60.00
EP 10.00
CE 25.00
CXP 12.00

END OF INSTRUMENT CONTROL PARAMETERS

==
AGILENT 1200 SERIES LC PARAMETERS
==

Agilent LC Pump Method Properties

Pump Model:	Agilent 1200 Binary Pump
Minimum Pressure (psi):	0.0
Maximum Pressure (psi):	5801.0
Dead Volume (µl):	40.0
Maximum Flow Ramp (ml/min^2):	100.0
Maximum Pressure Ramp (psi/sec):	290.0

Step Table:

@Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	1.00	200	50.0	50.0
1	7.00	200	50.0	50.0

Left Compressibility:	50.0
Right Compressibility:	115.0
Left Dead Volume (µl):	40.0
Right Dead Volume (µl):	40.0
Left Stroke Volume (µl):	-1.0
Right Stroke Volume (µl):	-1.0
Left Solvent:	A2
Right Solvent:	B2

Agilent Autosampler Properties

Autosampler Model:	Agilent 1200 High Performance Autosampler
Syringe Size (µl):	100
Injection Volume (µl):	4.00
Draw Speed (µl/min):	200.0
Eject Speed (µl/min):	200.0
Needle Level (mm):	0.00
Temperature Control	Not Used
Wash Location:	Wash Vial
Wash Cycles (1 - 5):	2
Wash Vial Number:	1
Wash Rack Number:	1

Automatic Delay Volume Reduction	Not Used
Equilibration Time (sec):	2
Enable Vial/Well Bottom Sensing	No
Use Custom Injector Program	No

Agilent Column Oven Properties

Left Temperature (°C):	25.00
Right Temperature (°C):	25.00
Temperature Tolerance +/- (°C):	10.00
Start Acquisition Tolerance +/- (°C):	5.00
Time Table	(Not Used)
Column Switching Valve	Installed
Position for first sample in the batch:	Left

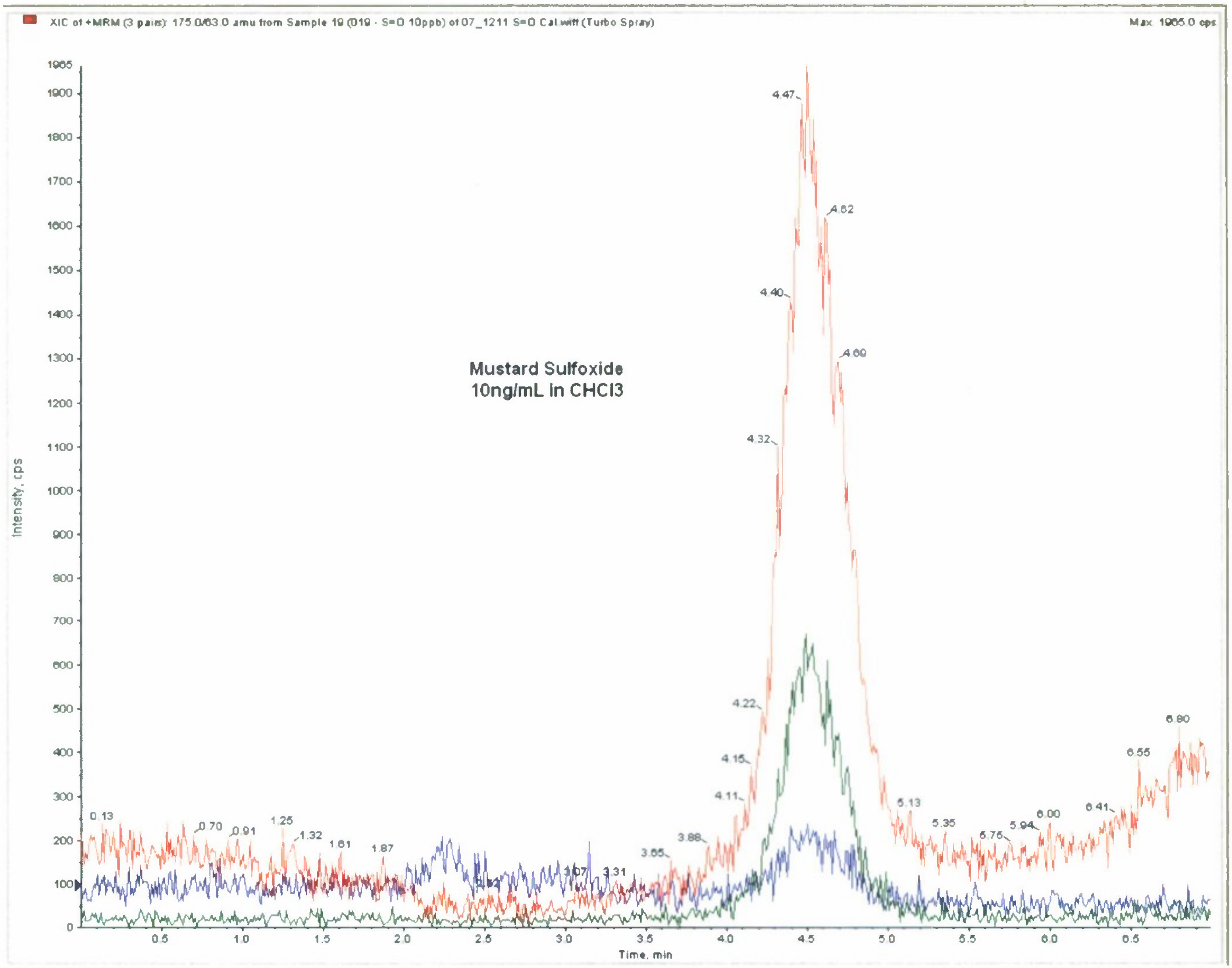
Use same position for all samples in the batch

Column Type:
Agilent ZORBAX
SB-C18
PN: 866953-902
SN: USDZ010845
4.6mm x 75mm 3.5μm

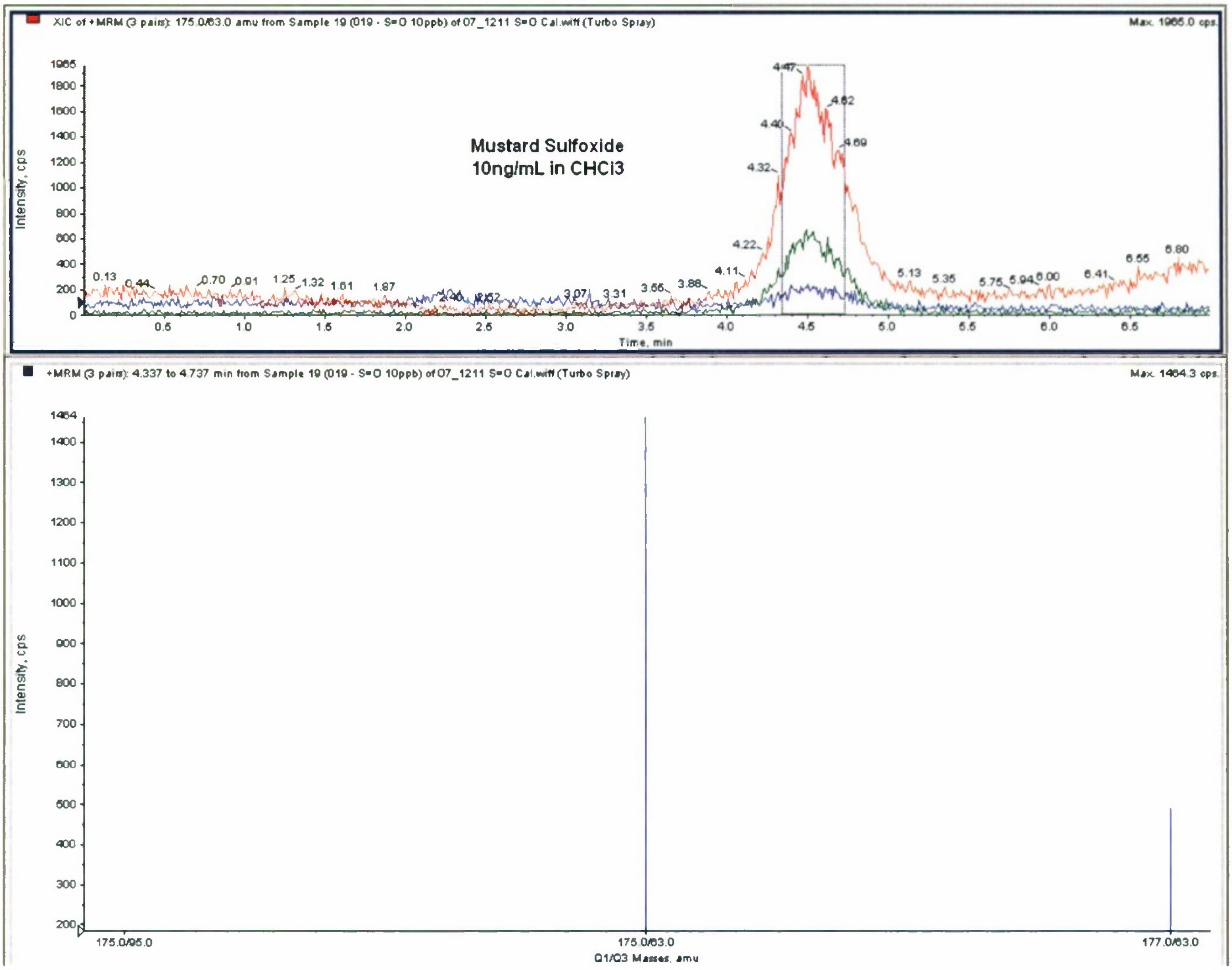
Mobile Phase
Aqueous:
95% dH20
5% Acetonitrile
0.1% Formic Acid
5mM Ammonium Acetate

Organic:
95% Acetonitrile
5% dH20
0.1% Formic Acid
5mM Ammonium Acetate

H-Sulfoxide Chromatogram - 408-LCE DATA ANALYSIS



H-Sulfoxide MS/MS Spectrum - 408-LCE DATA ANALYSIS



METHOD N: GC-MS METHOD FOR HD SULFONE IDENTIFICATION (GCE H-SULFONE_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of Mustard agent (HD) and the oxidation by-product of HD, Mustard Sulfone (H-Sulfone) in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with Autosampler.

AUTHORS
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Mustard, HD, Bis(2-chloroethyl)sulfide CAS 505-60-2
Mustard Sulfone, H-Sulfone, Bis(2-chloroethyl)sulfone, CAS 471-03-4

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and identify the chemical agent HD and H-Sulfone, the oxidation by-product of HD, in liquid extraction samples. This method is to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately four (4) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to identify the chemical agent HD and/or the HD by-product H-Sulfone when present independently or within the same sample. This method can detect and identify HD solution concentrations from approximately 2.0 to 2000 ng/mL. This method can identify H-Sulfone solution concentrations from approximately 10 to 2000 ng/mL.

The method performance for H-Sulfone is as follows:

- Qualitative Method
- Sample Solvent: chloroform.
- Quant Ion: 63.

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent chloroform ($CHCl_3$; CAS #67-66-3) and containing the chemical agent HD and/or the HD by-product H-Sulfone. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT
This document does not claim to address all of the safety concerns associated with chemical decontaminant testing as the requirements may vary based on facility, state and other

regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte(s) of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute HD and H-Sulfone standards prepared in high purity chloroform solvent. Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                          "H-Sulfone_Deans.M"
                        ECBC Decon Sciences Team
                         408-GCE Method Summary

        INSTRUMENT CONTROL PARAMETERS:    GCE (6890GC - 5975MSD)
        --------------------------------------------------------
D:\GC-MS METHODS\H-Sulfone_Deans.M

Control Information
------- -----------
Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes


==========================================================================
                    AGILENT DEANS SWITCH PARAMETERS
==========================================================================
METHOD: 408-GCE_Deans.M

     Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.

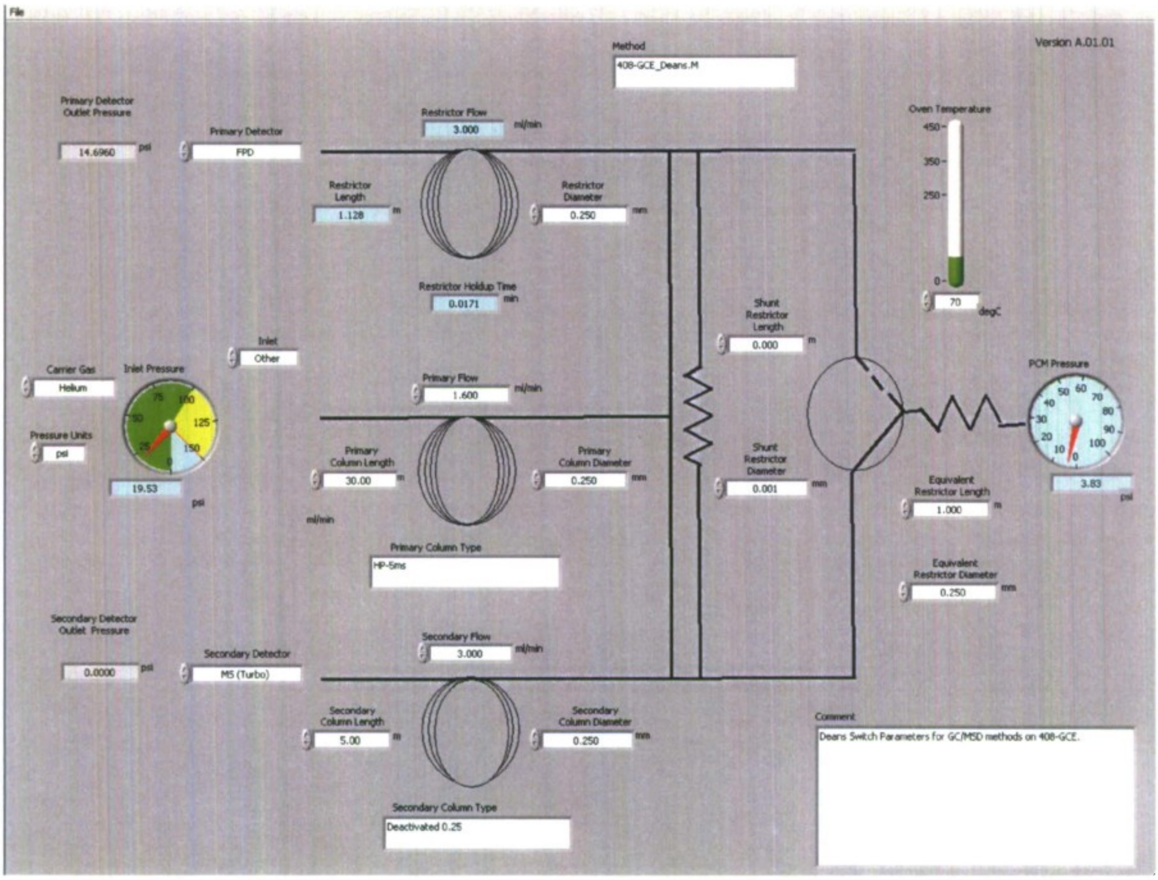
CALCULATION RESULTS:
                                  Primary Column   Secondary Column
```

Inlet Pressure:	19.53	3.83
Avg. Linear Velocity (cm/sec):	34.72	154.76
Hold up Time (min):	1.44	0.054
Restrictor Length (m):		1.128
Restrictor Hold Up Time (min):		0.017

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	5.00
i.d. (MM):	0.25	0.25
Flow (ml/min):	1.60	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70.00
Restrictor Diameter:		0.25
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR



==

GERSTEL CIS

==

```
TEMPERATURE PROGRAM
Initial Temperature      : 10 'C
Equilibration Time       : 0.05 min
Initial Time             : 0.20 min
Ramp 1
Rate 1               : 10.0 'C/s
End Temp 1           : 280 'C
Hold Time 1          : 3.00 min
Ramp 2
Rate 2               : 0.0 'C/s

CRYO COOLING
Cryo Cooling             : used

GERSTEL MPS Liquid Injection

Syringe                  : 10ul

SAMPLE PARAMETERS
```

```
Inj. Volume             : 2.0 uL
Inj. Speed              : 25.00 uL/s
Fill Volume             : 10.0 uL
Fill Strokes            : 3

Fill Speed              : 5.00 uL/s
Eject Speed             : 100.00 uL/s
Viscositiy Delay        : 1.0 s

Air Volume              : 0.0 uL
Pre Inj. Delay          : 0.00 s
Post Inj. Delay         : 0.00 s
Inj. Penetration        : 40.00 mm
Vial Penetration        : 31.00 mm

CLEANING PARAMETERS
Preclean Sample         : 0

Preclean Solv.1         : 1
Postclean Solv.1        : 3
Fill Speed Solv.1       : 5.00 uL/s
Viscosity Delay Solv.1  : 1.0 s
Eject Speed Solv.1      : 100.00 uL/s

Preclean Solv.2         : 1
Postclean Solv.2        : 3
Fill Speed Solv.2       : 5.00 uL/s
Viscosity Delay Solv.2  : 1.0 s
Eject Speed Solv.2      : 100.00 uL/s

========================================================================
                              6890 GC METHOD
========================================================================
OVEN
Initial temp:  70 'C (On)               Maximum temp:  325 'C
Initial time:  0.75 min                 Equilibration time:  0.25 min
Ramps:
#  Rate  Final temp  Final time
1 35.00      120        0.00
2 10.00      150        0.00
3 40.00      300        1.07
4   0.0(Off)
Post temp:  70 'C
Post time:  0.00 min
Run time:  10.00 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (CIS3)
Mode:  Split                            Mode:  Solvent Vent
Initial temp:  200 'C (Off)             Initial temp:  250 'C (Off)
Pressure:  0.00 psi (Off)               Pressure:  19.53 psi (On)
Total flow:  3.7 mL/min                 Vent time:  0.20 min
Gas saver:  Off                         Vent flow:  20.0 mL/min
Gas type:  Helium                       Vent Pressure:  19.5 psi
                                         Purge flow:  50.0 mL/min
                                         Purge time:  3.00 min
```

Total flow: 54.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium
Initial pressure: 3.80 psi (On)
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

AUX PRESSURE 5
Description:
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

VALVES
Valve 1 Switching Off
Description:

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
5.00	Valve 1:	On
6.00	Valve 1:	Off
7.00	Valve 1:	On
8.00	Valve 1:	Off

GC Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number : AB001
Column 2 Inventory Number : AB002

===
5975 MS ACQUISITION PARAMETERS
===

General Information
------- -----------
Tune File : atune.u
Acquistion Mode : SIM

MS Information
-- -----------
Solvent Delay : 5.00 min

EM Absolute : False
EM Offset : 400
Resulting EM Voltage : 2400.0*

[Sim Parameters]

GROUP 1
Group ID : HD
Resolution : High
Plot 1 Ion : 109.00
Ions/Dwell In Group:

(Mass, Dwell)
(109.00, 75)

```
(111.00, 75)
(158.00, 75)
(160.00, 75)

GROUP 2
Group ID                    : HD
Resolution                  : High
Group Start Time            : 6.50
Plot 1 Ion                  : 27.00
Ions/Dwell In Group:

(Mass, Dwell)
(27.00, 75)
(28.00, 75)
(63.00, 75)
(65.00, 75)

[MSZones]
MS Quad                     : 150 C   maximum 200 C
MS Source                   : 230 C   maximum 250 C
Timed Events
----- ------

[Timed MS Detector Entries]

END OF MS ACQUISITION PARAMETERS
```

TUNE PARAMETERS*

**MSD Specific Values automatically determined and set when performing an Autotune.*

```
END OF TUNE PARAMETERS
-------------------------------------

END OF INSTRUMENT CONTROL PARAMETERS
-------------------------------------
```

HD SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Mustard Gas Formula: $C_4H_8Cl_2S$ MW: 158
CAS#: 505-60-2 NIST#: 289463 ID#: 65664 DB: mainlib

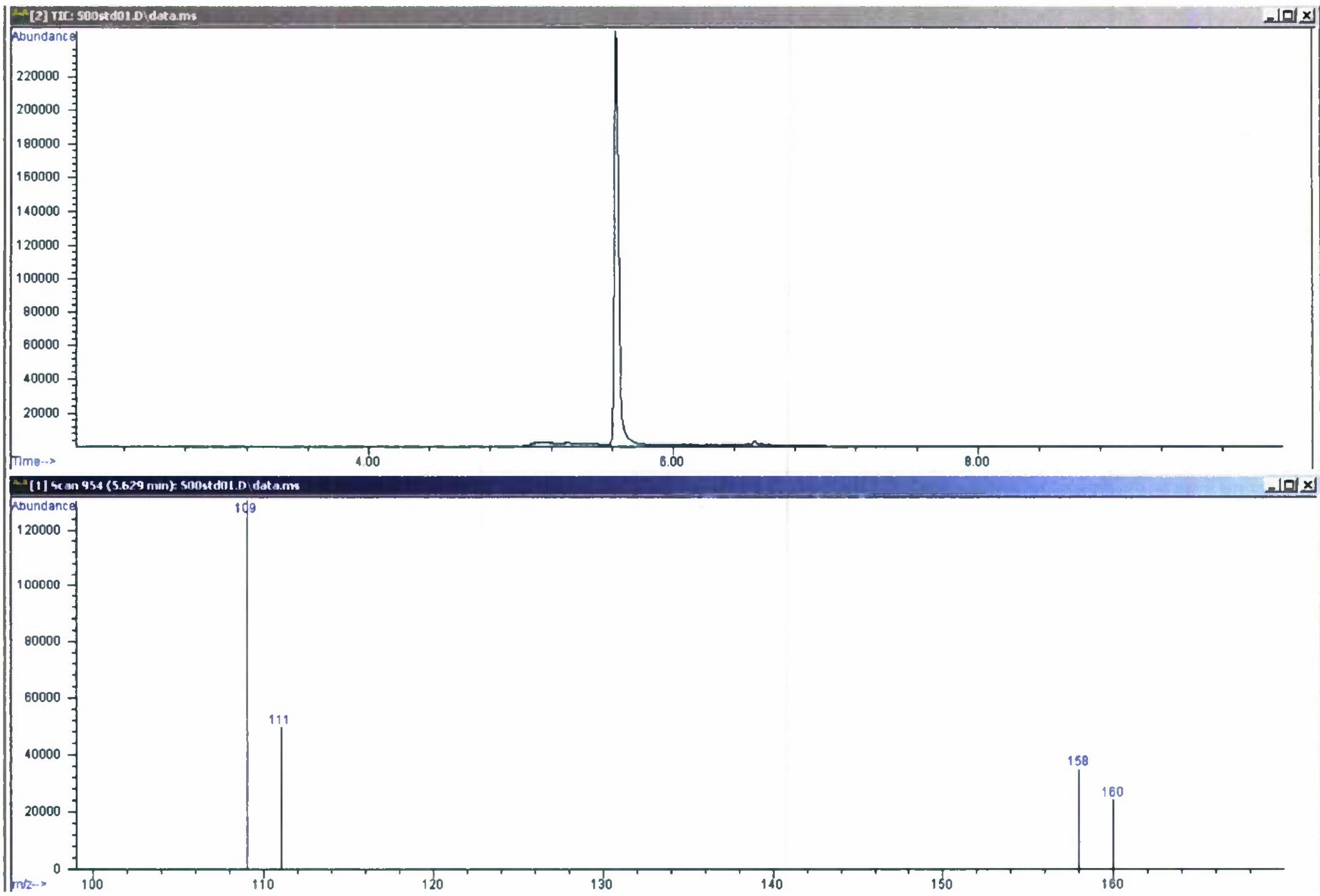
H-Sulfone SPECTRUM (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Bis(á-chloroethyl) sulfone Formula: $C_4H_8Cl_2O_2S$ MW: 190
CAS#: 471-03-4 NIST#: 289499 ID#: 75 DB: mainlib

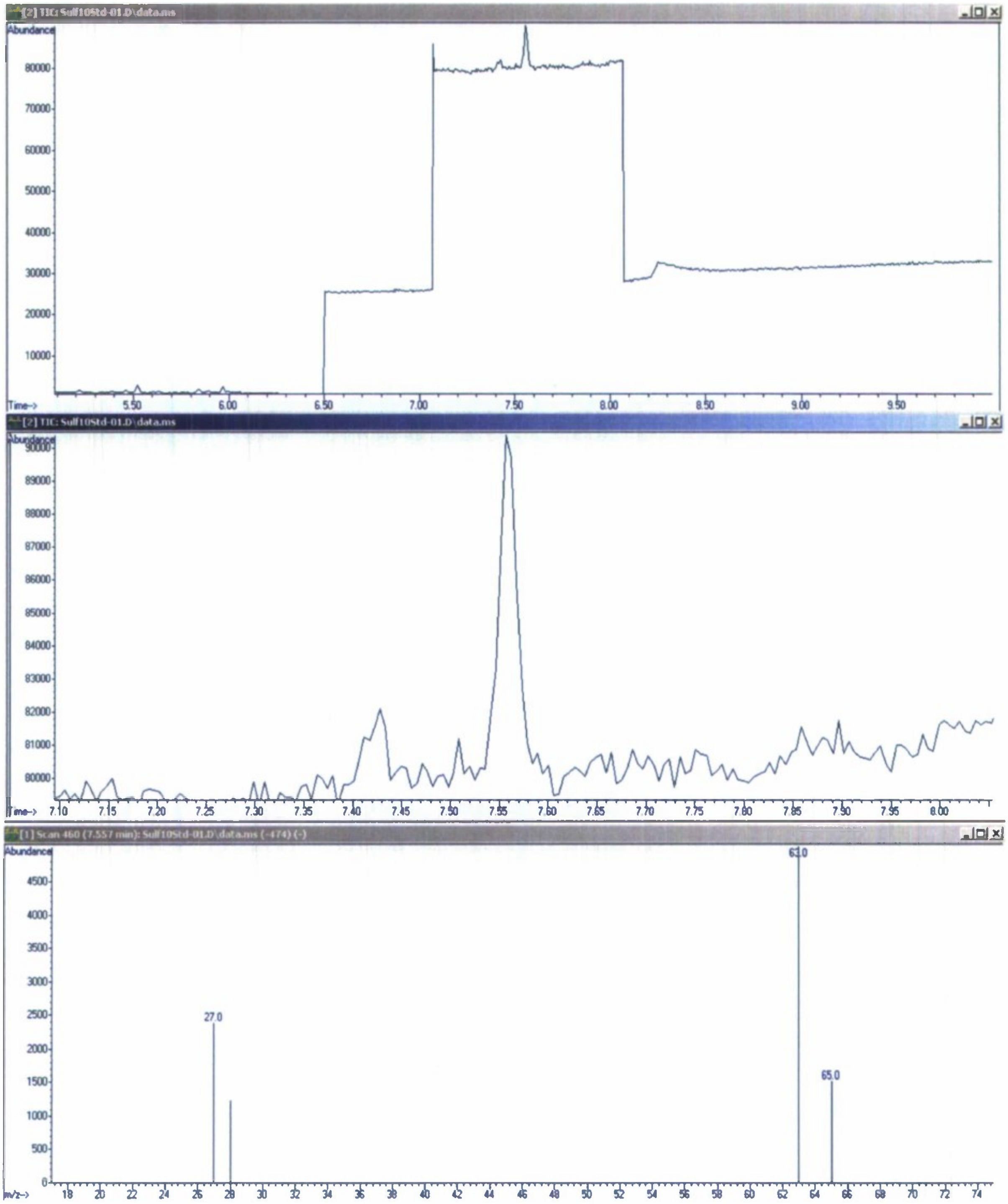
A sample spectrum from this program is provided.

HD TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



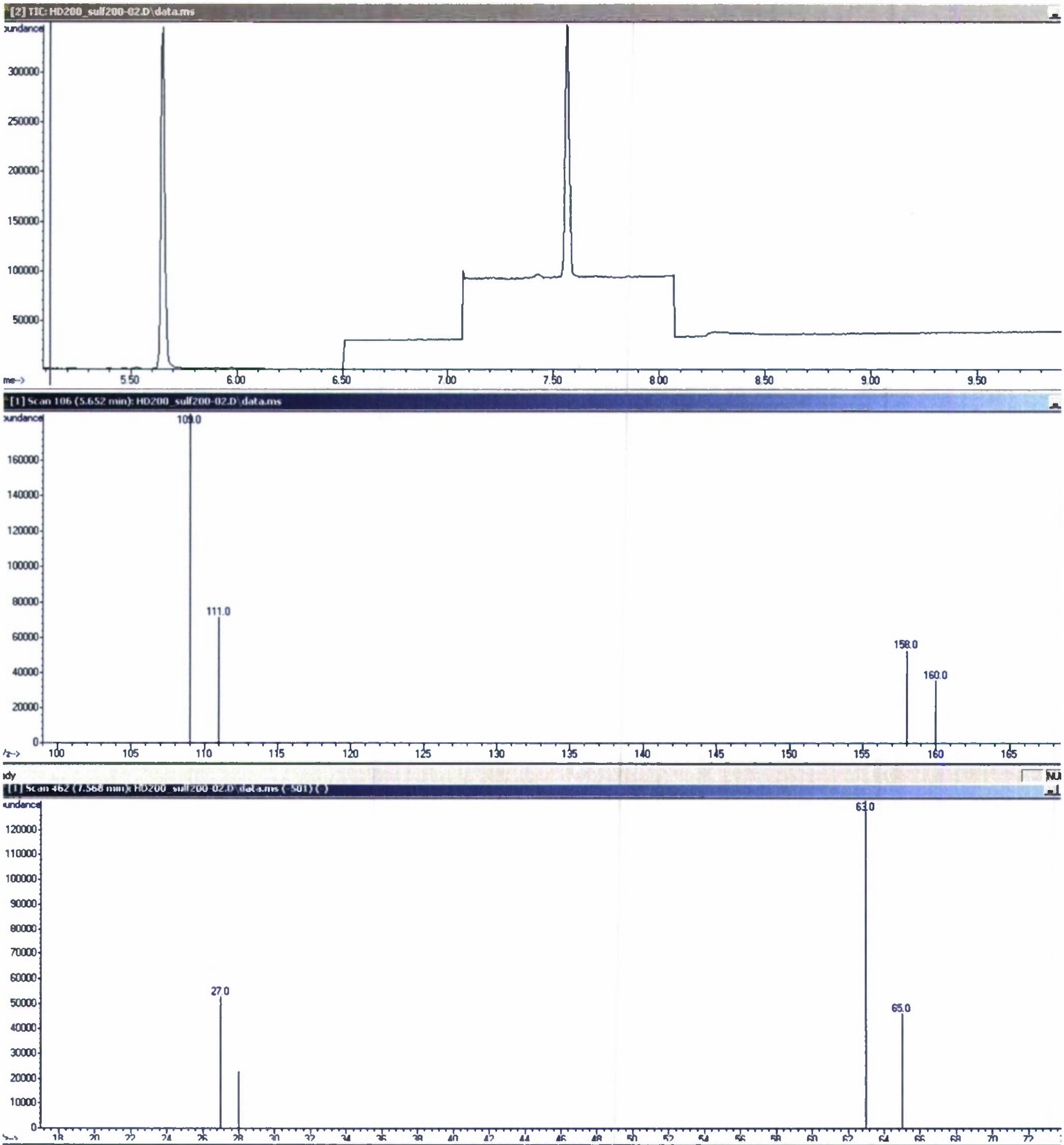
Approximate Method retention time for HD: 5.63 minutes.

H-Sulfone TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS

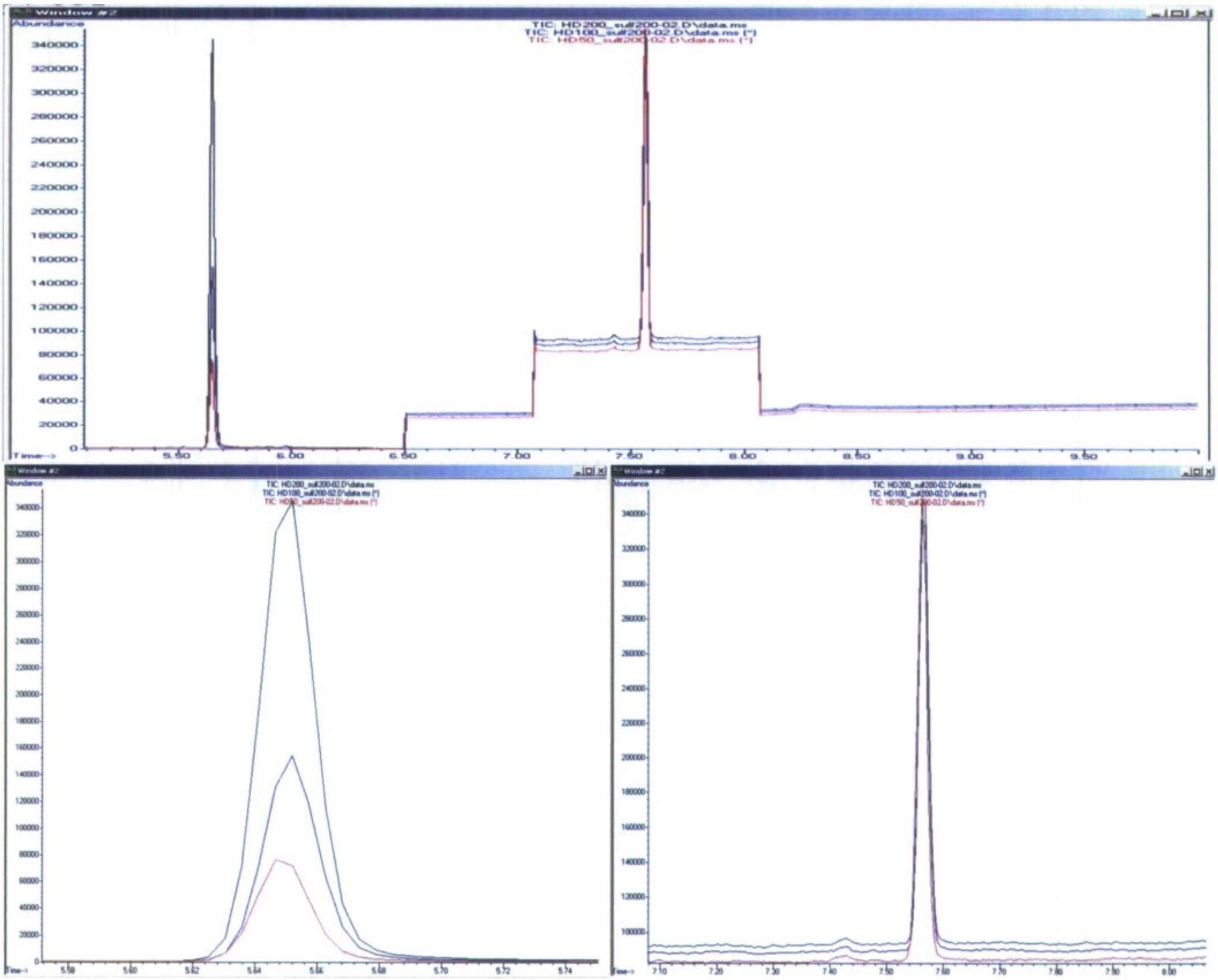


Approximate Method retention time for H-Sulfone: 7.56 minutes.

HD and H-Sulfone TIC and Spectrum (SIM) - 408-GCE DATA ANALYSIS



HD and H-Sulfone Overlays of Multiple HD Concentrations
408-GCE DATA ANALYSIS



A. (Top)Overlays of HD and H-Sulfone
B. (Bottom, left) Zoom of varying concentrations of HD
C. (Bottom, right)Zoom of same concentration H-Sulfone

METHOD O: GC-MS METHOD FOR GD-ACID IDENTIFICATION (GCE GD-ACID_DEANS.M)

ANALYTICAL METHOD

TITLE
Detection of the hydrolysis by-product of GD, Pinacolyl Methylphosphonic Acid (GD-Acid) in liquid extraction samples for chemical agent decontamination testing using a GC/MSD with Autosampler.

AUTHORS
Matt Shue (SAIC)
Teri Lalain, Ph.D. (Team Leader, Decon Sciences)

KEYWORDS
Pinacolyl Methylphosphonic Acid, GD-Acid, Pinacolyl Methylphosphonate CAS 616-52-4

REVISION HISTORY
This document is version 1 released December 2007.

PURPOSE AND APPLICATIONS
The purpose of this method is to detect and identify the hydrolysis by-product of GD, Pinacolyl Methylphosphonic Acid (GD-Acid), in liquid extraction samples. This method is optimized to support the analysis of liquid extracts following the chemical agent decontamination performance evaluation testing for contact sampler and coupon extracts for a two-inch diameter test surface area extracted in no greater than 20 mL of extraction solvent. Sample throughput is approximately six (6) samples per hour.

ANALYTE CONCENTRATION RANGE
This method was developed to identify the GD by-product GD-Acid. This method can detect and identify GD-Acid solution concentrations from approximately 5,000 to 500,000 ng/mL. NOTE: Due to the large concentrations required, this method is not appropriate for analyzing GD and GD-Acid simultaneously.

The method performance for GD-Acid is as follows:

- Qualitative Method
- Sample Solvent: acetonitrile.
- Quant Ion Pair: 97.

SAMPLE MATRICES AND INTERFERENCES
This method is appropriate for liquid samples extracted with the solvent Acetonitrile (CH_3CN; CAS #75-05-8) and containing the GD by-product GD-Acid. No significant method interferents have been identified. Users of this method should confirm that the test material and solvent are compatible prior to testing.

RISK AND SAFETY ASSESSMENT
This document does not claim to address all of the safety concerns associated with chemical

decontaminant testing as the requirements may vary based on facility, state and other regulatory requirements. It is the responsibility of the user of this method to establish appropriate environment, health and safety practices for the use of this method and handling of generated wastes in compliance with applicable regulations prior to use. Users of this method should conduct testing in appropriate facilities and follow proper laboratory practices including the use of appropriate personal protective equipment and material safety data sheets.

SCIENTIFIC BASIS

This method is based on gas chromatography and mass spectrometry techniques.

TRAINING

Users of this method must have basic skill level for analytical chromatography instrument operation, interpretation of mass-spectrometry results and associated wet lab techniques (e.g., sample dilution, standard preparation). Instrument training covering operation and maintenance of equipment is suggested.

APPARATUS

The liquid extraction samples are analyzed on an Agilent 6890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD). The GC is outfitted with an Agilent Deans Switch allowing for flow switching during analysis so that only a small portion of the sample effluent, including the analyte(s) of interest, is directed to the MSD. All other flow is directed to a flame photometric detector (FPD). Sample introduction is performed using a GERSTEL Multi Purpose Sampler (MPS2) and a GERSTEL cooled injection system inlet (CIS4). The system is fitted with a HP-5MS 5% Phenyl Methyl Siloxane column. Instrumentation operation and maintenance manuals are available from the instrument manufacturers: Agilent and GERSTEL. Miscellaneous and consumable equipment lists are also available from the manufacturer. All equipment should be used in accordance with manufacturer instructions.

Chemicals required include dilute GD-Acid standards prepared in high purity Acetonitrile solvent. Volumetric glassware used for standard preparation should be Class A and meet the specifications in the most current version of ASTM standards E288 and E69. Pipettes used for standard preparation should be compliant with the required performance specifications listed in the most current versions of ISO 8655 Parts 1 and 2 and/or ASTM E 1154 for the volume being measured if standards are made volumetrically. Balances used for gravimetric standard preparation should be sensitive enough to measure appropriate mass delivered. All equipment should be used in accordance with manufacturer's requirements, properly maintained and calibrated.

Amber glass analytical sample vials are preferred. The septum cap should be inert lined, PTFE / Teflon preferred, to prevent extraction of plasticizers or other impurities into the sample.

PROCEDURE

The specific equipment and column are identified in the "Apparatus" section. Procedures for equipment operation are found in the manufacturer operating manuals. The specific instrumentation settings for this method are provided in the "Method Parameters" section. Instrumentation problems and corrective actions are typically provided in the manufacturer operating manuals. The equipment should be confirmed operational prior to use for test support.

Standards are prepared either volumetrically or gravimetrically for the calibration required by the method.

Liquid extract samples above the method calibration range are diluted to be within the method calibration range as extrapolation of results outside the calibrated range is not recommended.

Calibration curves are generated from the standard sample results. The curves are fit and weighted as specified in this method. The analysis of test samples must include the use of initial calibration verification (ICV), continuing calibration verifications (CCV) and solvent blanks for quality control. Specific guidance for the use of these methods for decontaminant performance evaluations is provided in the "2007 Chemical Decontaminant Performance Evaluation Testing Source Document" by T. Lalain, et.al. Standard preparation, sample queues, interferences and other general analytical guidance are provided in the corresponding technical report to this document titled "Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations" by T. Lalain, et.al.

DATA ACCEPTANCE & REPORTING

Analytical results for samples are reported as solution concentrations (ng/ml). Solution concentration can be calculated in the instrument control software (e.g., Applied Biosystems Analyst, Chemstation, etc.) or in external statistical software (e.g., Excel, Sigma plot, etc.) using the specified calibration model. The reported solution concentration should account for sample dilutions made post original sample generation (e.g., contact, residual, remaining agent testing) such that the analyzed sample is within the calibration range. Calibration curves are not extrapolated; samples must fall within the range or be reported as 'above calibration range' or 'below detection' as appropriate. The reported concentration is acceptable if all QA/QC criteria are met as specified (e.g., CCVs before and after the sample are within 30% RSD).

METHOD PARAMETERS

```
                                 "GD-Acid_Deans.M"
                              ECBC Decon Sciences Team
                               408-GCE Method Summary

         INSTRUMENT CONTROL PARAMETERS:    GCE (6890GC - 5975MSD)
         --------------------------------------------------------
D:\GC-MS METHODS\GD-Acid_Deans.M

Control Information
------- -----------
Sample Inlet : GC
Injection Source : Manual
Injection Location : Rear
Use MS : Yes


=========================================================================
                      AGILENT DEANS SWITCH PARAMETERS
=========================================================================
METHOD: 408-GCE_Deans.M

     Comment: Deans Switch Parameters for GC/MSD methods on 408-GCE.
```

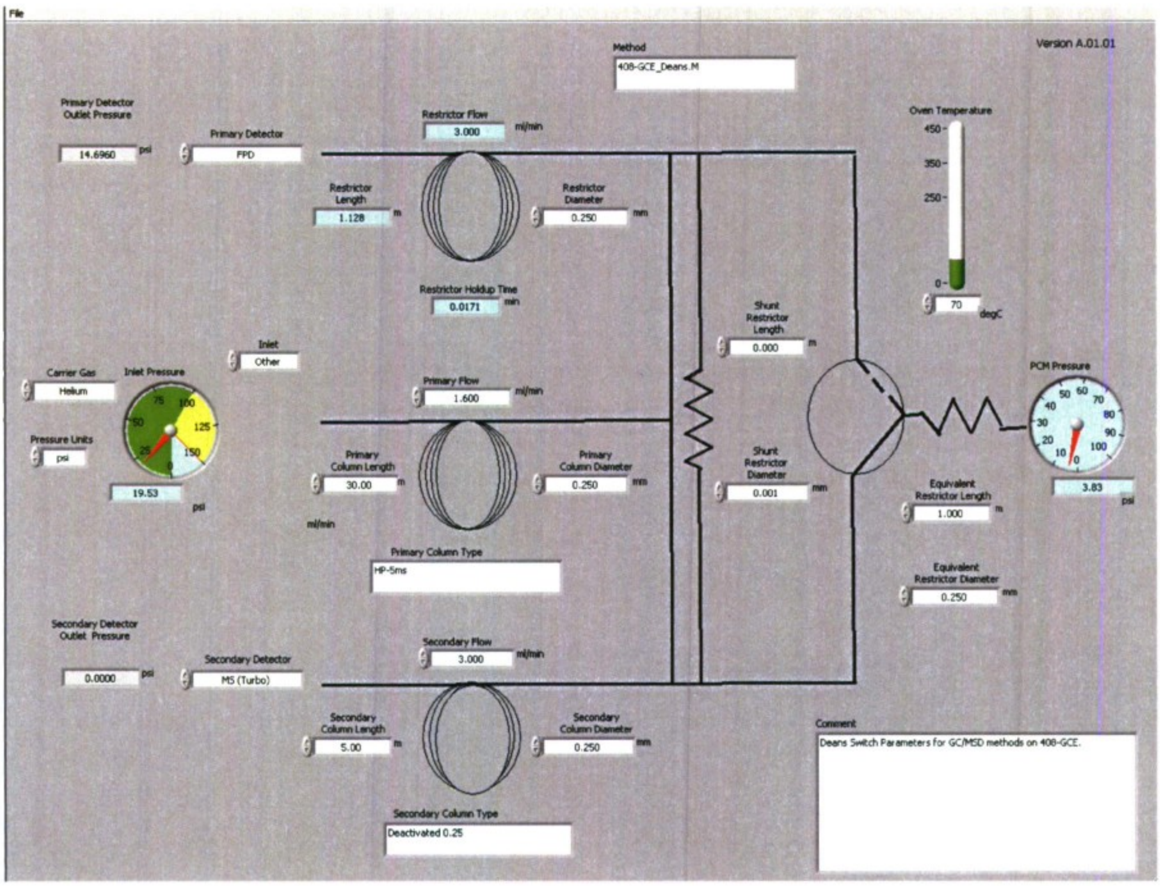
CALCULATION RESULTS:

	Primary Column	Secondary Column
Inlet Pressure:	19.53	3.83
Avg. Linear Velocity (cm/sec):	34.72	154.76
Hold up Time (min):	1.44	0.054
Restrictor Length (m):		1.128
Restrictor Hold Up Time (min):		0.017

CALCULATION INPUTS

	Primary Column	Secondary Column
Length (m):	30.00	5.00
i.d. (MM):	0.25	0.25
Flow (ml/min):	1.60	3.00
Detector:	FPD	MS (Turbo)
Detector Pressure (abs):	14.70	0.00
Carrier Gas:		Helium
Pressure Units:		psi
Oven Temperature:		70.00
Restrictor Diameter:		0.25
Equivalent Restrictor Diameter (mm):		0.25
Equivalent Restrictor Length (m):		1.000

DEANS SWITCH CALCULATOR




```
=========================================================================
                              GERSTEL CIS
=========================================================================
TEMPERATURE PROGRAM
Initial Temperature        : 50 'C
Equilibration Time         : 0.05 min
Initial Time               : 0.20 min
Ramp 1
Rate 1                 : 12.0 'C/s
End Temp 1             : 280 'C
Hold Time 1            : 3.00 min
Ramp 2
Rate 2                 : 0.0 'C/s

CRYO COOLING
Cryo Cooling               : used


GERSTEL MPS Liquid Injection

Syringe                    : 10ul
```

```
SAMPLE PARAMETERS
Inj. Volume               : 1.0 uL
Inj. Speed                : 25.00 uL/s
Fill Volume               : 10.0 uL
Fill Strokes              : 3

Fill Speed                : 5.00 uL/s
Eject Speed               : 100.00 uL/s
Viscositiy Delay          : 1.0 s

Air Volume                : 0.0 uL
Pre Inj. Delay            : 0.00 s
Post Inj. Delay           : 0.00 s
Inj. Penetration          : 40.00 mm
Vial Penetration          : 31.00 mm

CLEANING PARAMETERS
Preclean Sample           : 0

Preclean Solv.1           : 1
Postclean Solv.1          : 2
Fill Speed Solv.1         : 5.00 uL/s
Viscosity Delay Solv.1    : 1.0 s
Eject Speed Solv.1        : 100.00 uL/s

Preclean Solv.2           : 1
Postclean Solv.2          : 2
Fill Speed Solv.2         : 5.00 uL/s
Viscosity Delay Solv.2    : 1.0 s
Eject Speed Solv.2        : 100.00 uL/s


===========================================================================
                              6890 GC METHOD
===========================================================================
OVEN
   Initial temp:  70 'C (On)               Maximum temp:  325 'C
   Initial time:  0.75 min                 Equilibration time:  0.25 min
   Ramps:
      #  Rate  Final temp  Final time
      1 45.00      280        2.6
      2   0.0(Off)
   Post temp:  50 'C
   Post time:  0.00 min
   Run time:  8.02 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (CIS3)
   Mode:  Split                            Mode:  Solvent Vent
   Initial temp:  200 'C (Off)             Initial temp:  250 'C (Off)
   Pressure:  0.00 psi (Off)               Pressure:  19.53 psi (On)
   Total flow:  3.7 mL/min                 Vent time:  0.20 min
   Gas saver:  Off                         Vent flow:  20.0 mL/min
   Gas type:  Helium                       Vent Pressure:  19.5 psi
                                           Purge flow:  50.0 mL/min
```

Purge time: 3.00 min
Total flow: 54.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 19.53 psi
Nominal initial flow: 1.7 mL/min
Average velocity: 39 cm/sec
Inlet: Back Inlet
Outlet: Other
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Inlet: (unspecified)
Outlet: Other

FRONT DETECTOR (NO DET)

BACK DETECTOR (FPD)
Temperature: 250 'C (On)
Hydrogen flow: 75.0 mL/min (On)
Oxidizer flow: 100.0 mL/min (On)
Oxidizer Gas Type: Air
Mode: Constant makeup flow
Makeup flow: 25.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Lit offset: 2.00
Photo multiplier: On

SIGNAL 1
Data rate: 20 Hz
Type: back detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 1
Use: MSD Transfer Line Heater
Description: MSD Transferline
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

THERMAL AUX 2
Unknown Thermal Aux Type

AUX PRESSURE 3
Description: No vent
Gas Type: Helium
Initial pressure: 0.00 psi (Off)

AUX PRESSURE 4
Description: Deans Switch
Gas Type: Helium
Initial pressure: 3.80 psi (On)

```
                                                Initial time:  0.00 min
                                                   #  Rate  Final pres  Final time
                                                   1   0.0(Off)

AUX PRESSURE 5
   Description:
   Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)

VALVES                                         POST RUN
   Valve 1  Switching On                          Post Time: 0.00 min
      Description:

TIME TABLE
   Time        Specifier                        Parameter & Setpoint
      5.30        Valve 1:                         On
      6.30        Valve 1:                         Off


=============================================================================
                      5975 MS ACQUISITION PARAMETERS
=============================================================================
General Information
------- -----------
Tune File                  : atune.u
Acquistion Mode            : SIM

MS Information
-- -----------
Solvent Delay              : 5.00 min

EM Absolute                : False
EM Offset                  : 400
Resulting EM Voltage       : 2400.0*

[Sim Parameters]
GROUP 1
Group ID                   : GD-Acid
Resolution                 : High
Plot 1 Ion                 : 97.00
Ions/Dwell In Group
(Mass, Dwell)
(41.00, 75)
(80.00, 75)
(97.00, 75)
(124.00, 75)

[MSZones]
MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C
                      END OF MS ACQUISITION PARAMETERS


                              TUNE PARAMETERS*
                              ----------------
```

**MSD Specific Values automatically determined and set when performing an Autotune.*

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

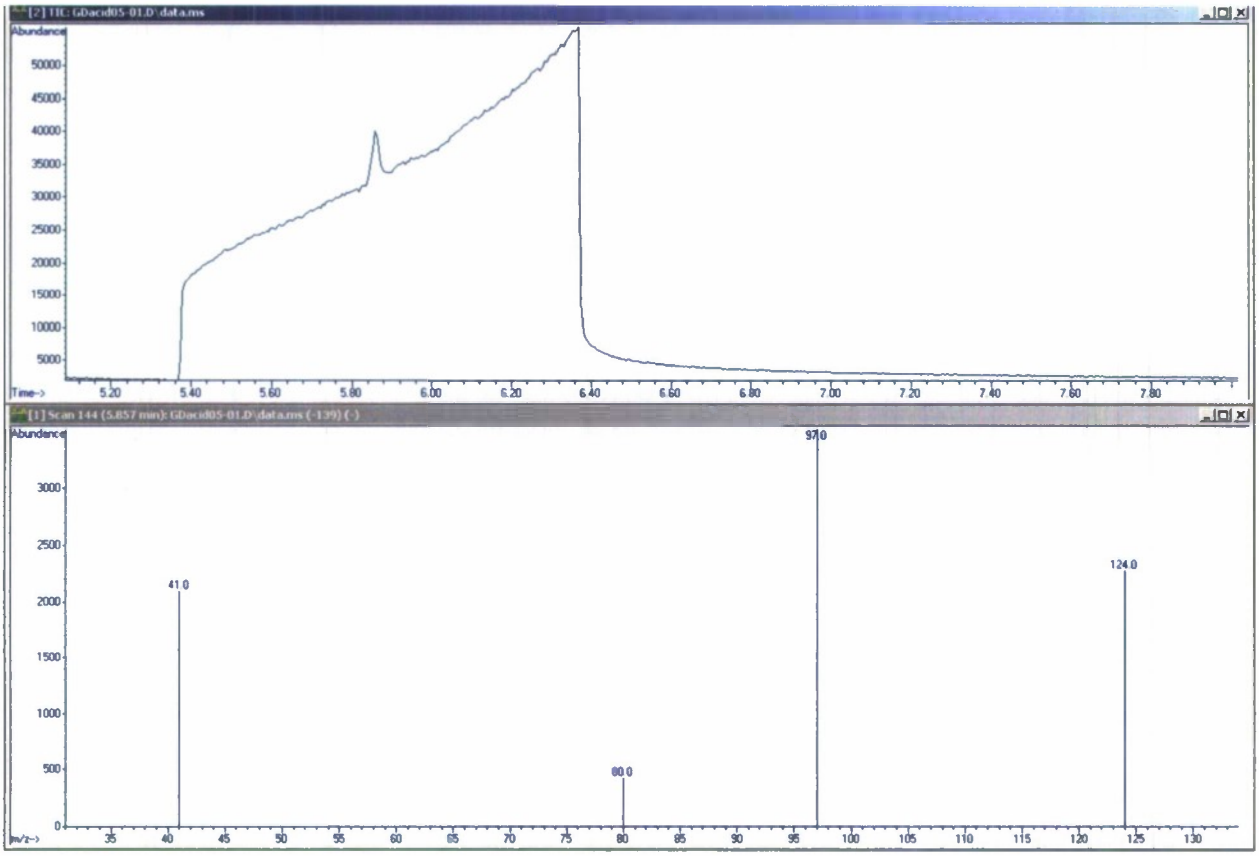
Pinacolyl Methylphosphonic Acid** (SCAN) - NIST LIBRARY SEARCH 2.0

The NIST library contains a sample spectrum which can be found as identified below:

Name: Methylphosphonic acid, 1,2,2,-trimethylpropyl ester Formula: $C_7H_{17}O_3P$
MW: 180 CAS#: 616-52-4 NIST#: 273479 ID#: 54739 DB: mainlib
**Identified in NIST Library by CAS Number.

A sample spectrum from this program is provided.

GD-Acid TIC and SPECTRUM (SIM) - 408-GCE DATA ANALYSIS



Approximate Method retention time for GD-Acid: 5.86 minutes.